(11) International Publication Number: WO 96/38223

(43) International Publication Date: 5 December 1996 (05.12.96)


Published

With international search report.

(54) Title: METHOD AND APPARATUS FOR GENERATION OF GAS LIQUID EMULSIONS WITH PREDETERMINED PHYSICAL AND CHEMICAL PROPERTIES

(57) Abstract

An apparatus and method for continuous, industrial scale generation of stable liquid-gas emulsions with predetermined physical and chemical characteristics for specific industrial waste flotation processes. A recycle reactor (54) is used to convert unstable gas-liquid dispersion (68) to a stable gas-liquid emulsion by a recycle action. Stable emulsion is removed via line (56) from the reactor (54) by a recycle pump (58) and directed to a centrifugal separator (66), which separates out a final emulsion product as an overflow stream (74), and returns a semi-emulsion (76) back to the reactor (54). The shearing or attrition caused by the impingement of the semi-emulsion (76) on the reactor contents (68) provides for the conversion of the unstable dispersion to stable emulsion. Control of the recycle action imparts desired characteristics to the final emulsion product. The unstable gas-liquid dispersion is preferably provided to the recycle reactor (54) by one or more preliminary bubble generating (38) and attrition (46) devices.
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>AM</td>
<td>Armenia</td>
<td>GB</td>
<td>United Kingdom</td>
<td>MW</td>
<td>Malawi</td>
</tr>
<tr>
<td>AT</td>
<td>Austria</td>
<td>GE</td>
<td>Georgia</td>
<td>MX</td>
<td>Mexico</td>
</tr>
<tr>
<td>AU</td>
<td>Australia</td>
<td>GN</td>
<td>Guinea</td>
<td>NE</td>
<td>Niger</td>
</tr>
<tr>
<td>BB</td>
<td>Barbados</td>
<td>GR</td>
<td>Greece</td>
<td>NL</td>
<td>Netherlands</td>
</tr>
<tr>
<td>BE</td>
<td>Belgium</td>
<td>HU</td>
<td>Hungary</td>
<td>NO</td>
<td>Norway</td>
</tr>
<tr>
<td>BF</td>
<td>Burkina Faso</td>
<td>IE</td>
<td>Ireland</td>
<td>NZ</td>
<td>New Zealand</td>
</tr>
<tr>
<td>BG</td>
<td>Bulgaria</td>
<td>IT</td>
<td>Italy</td>
<td>PL</td>
<td>Poland</td>
</tr>
<tr>
<td>BJ</td>
<td>Benin</td>
<td>JP</td>
<td>Japan</td>
<td>PT</td>
<td>Portugal</td>
</tr>
<tr>
<td>BR</td>
<td>Brazil</td>
<td>KE</td>
<td>Kenya</td>
<td>RO</td>
<td>Romania</td>
</tr>
<tr>
<td>BY</td>
<td>Belarus</td>
<td>KG</td>
<td>Kyrgyzstan</td>
<td>RU</td>
<td>Russian Federation</td>
</tr>
<tr>
<td>CA</td>
<td>Canada</td>
<td>KP</td>
<td>Democratic People’s Republic of Korea</td>
<td>SD</td>
<td>Sudan</td>
</tr>
<tr>
<td>CF</td>
<td>Central African Republic</td>
<td>KR</td>
<td>Republic of Korea</td>
<td>SE</td>
<td>Sweden</td>
</tr>
<tr>
<td>CG</td>
<td>Congo</td>
<td>KZ</td>
<td>Kazakhstan</td>
<td>SG</td>
<td>Singapore</td>
</tr>
<tr>
<td>CH</td>
<td>Switzerland</td>
<td>LI</td>
<td>Liechtenstein</td>
<td>SI</td>
<td>Slovenia</td>
</tr>
<tr>
<td>CI</td>
<td>Côte d’Ivoire</td>
<td>LK</td>
<td>Sri Lanka</td>
<td>SK</td>
<td>Slovakia</td>
</tr>
<tr>
<td>CM</td>
<td>Cameroon</td>
<td>LR</td>
<td>Liberia</td>
<td>SN</td>
<td>Senegal</td>
</tr>
<tr>
<td>CN</td>
<td>China</td>
<td>LT</td>
<td>Lithuania</td>
<td>SZ</td>
<td>Swaziland</td>
</tr>
<tr>
<td>CS</td>
<td>Czechoslovakia</td>
<td>LU</td>
<td>Luxembourg</td>
<td>TD</td>
<td>Chad</td>
</tr>
<tr>
<td>CZ</td>
<td>Czech Republic</td>
<td>LV</td>
<td>Latvia</td>
<td>TG</td>
<td>Togo</td>
</tr>
<tr>
<td>DE</td>
<td>Germany</td>
<td>MC</td>
<td>Monaco</td>
<td>TJ</td>
<td>Tajikistan</td>
</tr>
<tr>
<td>DK</td>
<td>Denmark</td>
<td>MD</td>
<td>Republic of Moldova</td>
<td>TT</td>
<td>Trinidad and Tobago</td>
</tr>
<tr>
<td>EE</td>
<td>Estonia</td>
<td>MG</td>
<td>Madagascar</td>
<td>UA</td>
<td>Ukraine</td>
</tr>
<tr>
<td>ES</td>
<td>Spain</td>
<td>ML</td>
<td>Mali</td>
<td>UG</td>
<td>Uganda</td>
</tr>
<tr>
<td>FI</td>
<td>Finland</td>
<td>MN</td>
<td>Mongolia</td>
<td>US</td>
<td>United States of America</td>
</tr>
<tr>
<td>FR</td>
<td>France</td>
<td>MR</td>
<td>Mauritania</td>
<td>UZ</td>
<td>Uzbekistan</td>
</tr>
<tr>
<td>GA</td>
<td>Gabon</td>
<td></td>
<td></td>
<td>VN</td>
<td>Viet Nam</td>
</tr>
</tbody>
</table>
METHOD AND APPARATUS FOR GENERATION OF GAS LIQUID EMULSIONS WITH PREDETERMINED PHYSICAL AND CHEMICAL PROPERTIES

Technical Field

The present invention pertains generally to devices and processes for generating unique foams and froths, and more particularly to a method and apparatus which can generate gas-liquid emulsions having specified physical and chemical properties on an industrial scale for use in flotation, foam fractionation, and other applications.

Background Art

Flotation techniques which employ suitable foams or froths have many applications in environmental cleanup, waste-treatment, mining, chemical, paper, food, and other industries. Froth flotation and foam fractionation/separation processes have great potential for removal of pollutants from industrial waste streams. Examples of the many pollutants and hazardous materials which may be treated by foam flotation processes include suspended minerals, food wastes, paper pulp, and sewage sludge, dissolved electroplating wastes such as chromates, dissolved organics such as dyes, solvents, oils and greases, bacteria, algae, plankton, and hazardous dissolved gases. Foam or froth flotation may also be employed in separation processes in the food, chemical and fermentation industries.

Several devices and methods for generation of foams, froths, or gas-liquid dispersions or emulsions are known. For example, U.S. Patent No. 5,314,644 discloses a microbubble generator which includes liquid and gas supply means, means for mixing the liquid and gas to form a coarse bubble dispersion, and means for shearing the coarse dispersion into a fine bubble dispersion. U.S. Patent No. 3,900,420 discloses microgas emulsions and a method of forming the same which creates a region of low pressure in a liquid flow through a venturi-type channel and entrains gas into the liquid in that region. U.S. Patent No. 3,048,272 and Canadian Patent No. 663,660 disclose a froth flotation process wherein a slurry is impelled into a liquid at a plurality of points along a predetermined path, thereby causing a froth to form. A device embodying this process is sold by Heyl & Patterson of Pittsburgh, Pennsylvania, under the name "Cyclo-Cell." Technology News, No. 281, July 1987, from the Bureau of Mines, U.S. Department of the Interior, disclosed an improved gas sparger system for column flotation wherein air and water are mixed in a glass bead-packed chamber to form a foam. U.S. Patent No. 3,645,892 discloses a method for aeration and foam separation employing a vortex element wherein a vortex valve is supplied with pressurized gas and liquid and provides a foam
output. The process of U.S. Patent No. 3,645,892 is further described by the Environmental Protection Agency, under Program Number 17030 FEB and Contract Number 14-12-863, February, 1972, which discloses a fluidic vortex bubble generation that provides bubbles which are transferred to a flotation tank.

Despite the tremendous potential of foam flotation for environmental cleanup, pollution treatment, and other applications, flotation techniques have seen little industrial implementation. The only significant industrial application heretofore has been in the mining industry, where flotation is used for separating and concentrating a variety of mineral products. The limited use of flotation processes has been due to several deficiencies in the presently available foam generating and flotation devices and processes. There is essentially no control, or knowledge of how to control, the size and quantities of bubbles generated in the aforementioned emulsion generating devices and methods, nor is there any ability to control the chemical and physical properties of bubbles and bubble surface films.

Similarly, there is very limited control of flotation conditions in the background art; e.g., the degree of turbulence within a flotation cell, the ratio of air to water, and the distribution of bubbles. The presently available foam flotation art is restricted as to the points of addition and manner of introduction of bubbles or foams into process streams, and flotation bubbles cannot be generated extraneous to the flotation cell because instability of the bubble dispersions prevents transportation of the bubbles.

One condition for ideal foam flotation is the ability to continuously and quantitatively generate bubbles of predetermined size, and with physical and chemical properties which are most effective for collecting and concentrating specific insoluble and soluble waste species in an aqueous medium under optimum generating conditions. Another such condition for ideal flotation is the ability to transport bubbles of predesigned size and properties in controlled quantities and introduce them to waste streams at the most advantageous points, thus minimizing turbulence and providing effective flotation.

Heretofore, the above ideal conditions have only been achieved in laboratory or small pilot plant scale operations. Previous efforts to scale up stable bubble, foam, or froth generation processes beyond a rate of about twenty five gallons per minute have been unsuccessful, and thus the treatment of industrial process streams and waste streams has been limited to stream volumes of about two hundred gallons per minute, which is too low for many industrial applications.

Accordingly, there is a need for an apparatus and method for generation of gas-liquid emulsions which provides stable, transportable, long-lived emulsions or foams having predetermined or predesigned physical and chemical properties, which produces gas-liquid emulsions at production rates suitable for industrial applications, which provides a gas-liquid emulsion which may be transported and
introduced to waste streams at the most advantageous points and under optimum conditions, and which can generate emulsions continuously. The present invention satisfies these needs, as well as others, and generally overcomes the deficiencies found in the background art.

The foregoing patents and publications reflect the state of the art of which the applicant is aware and are tendered with the view toward discharging applicant's acknowledged duty of candor in disclosing information which may be pertinent in the examination of this application. It is respectfully stipulated, however, that none of these patents teach or render obvious, singly or when considered in combination, applicant's claimed invention.

**Disclosure of Invention**

The invention disclosed herein pertains to an apparatus and method for continuous, industrial scale generation of stable, transportable gas-liquid emulsions having predetermined physical and chemical properties.

In general terms, the apparatus of the invention comprises recycle reactor means for converting an unstable gas-liquid dispersion into a stable gas-liquid emulsion, centrifugal means for separating or removing a final emulsion with predetermined chemical and physical characteristics from the stable emulsion as an overflow stream and returning a semi-emulsion to the reactor means as an underflow stream, and a recycle pump which directs the stable emulsion from the reactor means to the separating means. The recycle action of the semi-emulsion as it is returned to the reactor means provides a bubble shearing or attrition effect within the reactor means which produces the stable emulsion.

The output volume of final emulsion product produced by the invention is increased where a preliminary, unstable gas-liquid dispersion is produced by external bubble generating means and directed to the reactor means for conversion to the stable emulsion. Thus, the invention also preferably includes at least one preliminary bubble generating or bubble-shearing attrition means wherein relatively coarse, unstable gas-liquid dispersions are formed for addition to the reactor means. Supply means for providing and mixing liquid and gas for the preliminary bubble generating means are also preferably included.

By way of example and not of limitation, the recycle reactor means preferably comprises a reactor tank, in which bubble shearing or attrition is accomplished through a recycle action to produce a stable gas-liquid emulsion. The stable emulsion formed in the reactor means is then pumped by a recycle pump to centrifugal separation means wherein a final emulsion having specific, predetermined physical and chemical characteristics is continuously removed.
The recycle pump preferably comprises a positive displacement type pump having an impeller which provides additional bubble shearing during the recycle action. Vane or Moineau-type positive displacement pumps, as well as rotary displacement pumps, may also be employed as a recycle pump. The recycle pump rate preferably has a ratio in the range of between about two to one and about three to one with the working volume of the reactor means.

The separating means preferably comprises a centrifugal separator from which the final emulsion product is removed as an overflow product or stream, and a semi-emulsion underflow stream is continuously recycled or returned back to the reactor for further shearing action. The impingement of the semi-emulsion onto the reactor contents and the shearing action resulting therefrom provide the bubble attrition for producing a stable gas-liquid emulsion in the reactor. Preferably, the underflow to overflow rates have a ratio in the range of between about two to one and about four to one.

The final overflow product emulsion is uniform, stable and transportable and can be tailored in physical properties by selecting specific ratios of recycle pumping rate to reactor working volume, and specific ratios of underflow to overflow rates in the centrifugal separation means. Additional dewatering or liquid removal of the overflow emulsion may be carried out to remove excess liquid from the final emulsion.

The supply means preferably provides liquids by a feed pipeline, and includes means for adding surfactants or other ingredients to liquids and mixing therewith. The supply means generally includes pump means and a control valve and flow meter for the liquid. The supply means provides gas in the form of a pressurized tank, low pressure blower, or eductor, and may also include a flow meter and control valve. The supply means also generally includes means for mixing the liquid and gas provided.

The preliminary bubble generating and attrition means for producing coarse, unstable foams or dispersions may comprise static mixers, aspirators, eductors, bead columns, jets or other common foam generating means. The preliminary bubble generating and attrition means preferably are sequentially arranged in flow communication with each other, so that dispersions generated from one such preliminary bubble generating means are directed to a subsequent bubble generating means, and ultimately to the reactor means. Alternatively, the preliminary bubble generating means providing an unstable dispersion directly to the reactor means.

Use of preliminary bubble generating and attrition means in connection with the recycle reactor means and centrifugal separating means is an economical way of continuously producing large volumes of stable gas-liquid emulsion with desired properties. A series of stages of bubble generation or bubble grinding by the
preliminary bubble generating means, wherein each stage reduces the bubble size in 
an unstable dispersion from the previous stage, facilitates the final bubble grinding 
or bubble shearing which occurs in the recycle reactor means, thereby making 
higher volume outputs possible. Preferably, there are at least two preliminary 
bubble generating means included with the invention, with combined liquid and 
gas being supplied to a first preliminary bubble generating and attrition means 
wherein a first stage coarse, unstable gas-liquid dispersion or foam is formed. The 
first stage dispersion is directed to a second preliminary bubble attrition means 
wherein a second state dispersion, which is finer than the first stage dispersion, is 
formed and directed from the second preliminary bubble generating means to the 
recycle reactor means. Additional preliminary bubble generating means may be 
included for producing even finer unstable dispersions, depending upon the 
particulate application of the final emulsion and the volume output requirement 
required.

The method embodied by the present invention generally includes the steps 
of providing or supplying liquid and gas, adding surfactants or other additives to 
the liquid and mixing therewith, mixing of the gas and liquid, forming a relatively 
coarse, unstable gas-liquid dispersion in one or more stages, directing the unstable 
dispersion to recycle reactor means and forming a stable gas-liquid emulsion 
therein, and separating out a final emulsion product of predetermined 
characteristics from the stable emulsion and returning semi-emulsion to the reactor 
means.

**Industrial Applicability**

The industrial applicability of this invention shall be demonstrated through 
discussion of the following objects of the invention.

An object of the invention is to provide an apparatus and method for 
generating designed, uniform, stable, transportable gas-liquid emulsions.

Another object of the invention is to provide an apparatus and method for 
generating gas-liquid emulsions which provides specific desired physical and 
chemical properties required to clean a specific industrial waste stream.

Another object of the invention is to provide an apparatus and method for 
generating gas-liquid emulsions which allows continuous emulsion generation at 
volume rates greater than twenty-five gpm.

Another object of the invention is to provide an apparatus and method for 
generating gas-liquid emulsions which is simple, involves inexpensive equipment, 
and has minimal labor requirements and energy consumption.

Another object of the invention is to provide an apparatus and method for 
generating gas-liquid emulsions which has a small spatial requirement.
Another object of the invention is to provide an apparatus and method for generating gas-liquid emulsions which provides stable, transportable emulsion in quantities or volumes capable of treating industrial scale waste streams.

Another object of the invention is to provide an apparatus and method for generating gas-liquid emulsions which operates at ambient temperatures and pressures.

Another object of the invention is to provide an apparatus and method for generating gas-liquid emulsions which generates no hazardous byproducts or working conditions.

Further objects of the invention will be brought out in the following portions of the specification wherein the detailed description is for the purpose of fully disclosing the invention without placing limits thereon.

**Brief Description of Drawings**

The invention will be more fully understood by reference to the following drawings which are for illustrative purposes only:

Figure 1 is a schematic diagram of an apparatus for generation of gas-liquid emulsions in accordance with the invention.

Figure 2 is a schematic diagram of an alternative embodiment of the reactor and second bubble generator portion of the apparatus shown in figure 1.

Figure 3 is a flow diagram which shows generally the steps of the method comprising the present invention.

**Best Mode(s) For Carrying Out The Invention**

Referring more specifically to the drawings, for illustrative purposes the present invention is embodied in the apparatus which is generally shown in figure 1 and figure 2, and the method generally outlined in figure 3. It will be appreciated that the apparatus may vary as to configuration and as to details, and the method may be varied as to details and order of the steps as disclosed without departing from the basic concepts related herein.

Referring first to figure 1, the preferred embodiment of the present invention for continuously generating gas-liquid emulsions having predetermined or predesigned physical and chemical characteristics is shown generally as apparatus 10. The apparatus 10 includes an external supply means for providing liquid and gas, which preferably includes liquid feed line or pipe 12. As used in this disclosure, the term "line" generally refers to any form of pipe, channel, duct, passage, tube, or other means commonly used for transportation of liquids and gases and which can provide flow communication for fluids between various devices. Line 12 is connected with a liquid supply tank or pipe (not shown). Means for adding surfactants and other chemical additives to the liquid are generally included with
the supply means, preferably in the form of an eductor, static mixer, or mix tank, shown generally as mix station 14 on liquid feed line 12. The liquid supply means preferably includes a pump 16 connected to mix station 14 by line 18, with pump 16 directing liquid along line 20 to control valve 22, and hence to flow meter 24 along line 26. Pump 16, control valve 22 and flow meter 24 aid in controlling liquid supply rates and pressure to the apparatus 10. The invention is suitable for use with a variety of liquids which may form emulsions with gases, including water, gasoline, fuel oil or other liquid hydrocarbon fuels, solvents and solvent mixes, beers, wines or other alcoholic beverages, sea water, vegetable oils, fruit and vegetable juices, and other liquid food materials. Similarly, a large number of different surfactants and chemical additives are contemplated for addition to and mixing with such liquids, depending upon the particular flotation process for which the present invention is used. Typically, some form of anionic, cationic, or neutral surfactant, or combinations thereof, will be included in the liquid supply to aid in forming and stabilizing the gas liquid emulsion subsequently produced. For example, straight chain alkyl carboxylic acids, sulphates, sulphonates, phosphates, amines, and salts thereof, with chain lengths of ten to eighteen carbon atoms are typical surfactants which may be used with the present invention. Polymeric surfactants such as polyethylene glycols (PEG), polysorbates, and polyacid salts, may also be employed as surfactants. Chemical additives may include buffers, pH modifiers, salts, flocculating agents, or particular chemical reagents for particular flotation applications.

The supply means also provides gas, as shown in figure 1 by gas feed line 28, which is in flow communication with a pressurized gas tank or low pressure blower (not shown). Gas is directed along feed line 28 to flow meter 30 and through line 32 to mixer 34 wherein gas and liquid are mixed together, with liquid reaching mixer 34 through line 36 which receives liquid from flow meter 24. Mixer 34 is preferably a mixing "T" or other standard means for mixing gas and liquid which is commonly used in the art. Where air is used in forming emulsions, the supply means may employ an eductor as mixer 34 for mixing air with liquid from line 36. It is contemplated however, that the present invention may be employed for generating gas-liquid emulsions with a variety of gases. For example, carbon dioxide or nitrogen may be employed for generating fire-retardant or non-oxidizing emulsions or with hydrocarbons to avoid mixing oxygen with the hydrocarbons and thus reducing the risk of fire or explosion. Alternatively, air or oxygen may be used in emulsions with hydrocarbons to prepare oxygenated fuel foams for injection into furnaces or engines. Other gases, including methane or natural gas, chlorine, sulfur dioxide and hydrogen sulfide can be employed where required for particular foam or flotation applications.
The invention preferably employs a plurality of preliminary bubble generating and attrition means for producing a preliminary, relatively coarse, unstable gas-liquid dispersion or dispersions prior to generating a final or stable gas-liquid emulsion. The preliminary bubble generating means may comprise any of a variety of bubble shearing or bubble grinding devices, including static mixers, aspirators, eductors, bead columns, jets, or any other bubble-forming or foam generating means commonly used in the art. The preliminary bubble generating means produce relatively coarse, unstable dispersions having relatively large bubble diameters (500 to 2000 microns). The preliminary dispersions are subsequently converted to a stable gas-liquid emulsion as related below.

In the preferred embodiment, there are two bubble grinding or bubble shearing devices to serve as preliminary bubble generating and attrition means. A first preliminary bubble grinding device 38, which receives mixed gas and liquid from mixer 34 via line or pipe 40 at relatively low pressures, produces a first stage, coarse, unstable gas-liquid dispersion. Generally, the gas-liquid mix is received from line 40 at pressures which are typically in the range of ten to twenty-five psig. The first stage coarse dispersion is then directed from the first stage device 38 through lines 42 and 44 to a secondary preliminary bubble attrition means or bubble grinder device 46, wherein the first stage dispersion undergoes further shearing to form a second stage dispersion which, like the first stage dispersion, is generally coarse and unstable.

Additional gas may be added to the second stage bubble grinding device 46. Preferably, the added gas is excess gas recycled through pipe line 48 from subsequent portions of the apparatus 10, and is delivered to an eductor 50 along line 44, with eductor 50 receiving first stage dispersion from first stage bubble grinder 38 via line 42, and eductor 50 delivering the first stage unstable dispersion, together with any additional gas, to second stage bubble grinder 46 through line 44.

Additional preliminary bubble grinding or bubble shearing devices may be employed with the invention to form third and higher preliminary stages of dispersion, if required for a particular application.

The second stage unstable gas-liquid dispersion is delivered along line 52 directly to a recycle reactor means for converting unstable gas-liquid dispersion into a stable gas-liquid emulsion. The recycle reactor means is preferably in the form of a recycle reactor tank 54 which, in the embodiment shown in figure 1, serves as a third bubble shearing or grinding device and produces a stable or third stage emulsion wherein a major portion of the unstable gas-liquid dispersion from the preliminary bubble generating and attrition means is converted into a stable emulsion having a desired bubble size distribution and gas content. The bubble size, gas content, and physical characteristics generally of the stable emulsion are
controlled by the operating conditions of the reactor 54 and the recycle action as related below. The desired froth characteristics are imparted to the final emulsion by the shearing of the recycle action in reactor 54, as discussed more fully below.

The stable emulsion produced in reactor 54 is removed from reactor 54 through line 56 by the action of recycle pump 58. Recycle pump 58 is preferably a positive displacement type pump such as a rotary displacement pump which includes impeller pumping means. The impeller action in pump 58 provides further shearing to the stable emulsion from reactor tank 54. Positive displacement pumps available from Jabsco and Flowtech are suitable for use as a recycle pump 58 with the present invention.

Recycle pump 58 directs the stable emulsion from reactor 54 through line 60, control valve 62, and line 64 to a centrifugal means for separating and removing a final emulsion with predesigned physical and chemical characteristics from the stable emulsion and returning a semi-emulsion to reactor 54. The separating means is preferably in the form of a centrifugal separator 66, which removes a final emulsion product as an overflow stream and returns or recycles a semi-emulsion back to reactor 54 as an underflow stream. Additional bubble shearing or attrition occurs within separator 66. The semi-emulsion provides bubble shearing or bubble attrition to the contents of reactor 54 as the semi-emulsion is recycled or returned to reactor 54.

In order to produce a stable emulsion in reactor 54 the preferred operating conditions for reactor 54 and recycle pump 58 require that recycle pump 58 have a pumping capacity or pump rate which is two to three times greater than the working volume of reactor 54. For example, where the recycle pump rate is 100 gpm, reactor 54 has a working volume in the range of thirty to fifty gallons. In other words, the ratio of the recycle pump rate or capacity to the reactor working volume should preferably be within the range of between about two to one and about three to one. This particular recycle pump rate or capacity to reactor working volume ration range provides the recycle action, with its attendant shearing and attrition forces, necessary for production of stable gas-liquid emulsions with desired, predetermined or predesigned physical and chemical characteristics. Varying this ratio allows control of final bubble size ranges for varying applications. The recycle action is continuous, and is generally carried out at low working pressures or ambient pressure in reactor 54, but reactor 54 may be operated at higher pressures for particular applications wherein higher pressures are required for generating a stable gas-liquid emulsion. Excess gas in reactor 54 may be removed via line 48 to eductor 50 for re-use.

The liquid level or emulsion level 68 within reactor 54 is also important to generating a continuous output of stable emulsion, and thus the invention
includes means for sensing or monitoring and controlling the liquid level within reactor 54. The liquid level 68 generally defines the working volume of the reactor, and must be maintained at the appropriate level so that the ratio of the reactor working volume to the recycle pump rate remains within the preferred range related above. The working volume of reactor 54 is the portion of reactor 54 which is occupied by gas-liquid emulsion, and level 68 as shown in figure 1 is thus the interface between emulsion and gas or air within reactor 54. The amount of liquid present in reactor 54 controls the amount of emulsion, and thus controlling the amount of liquid entering reactor 54 controls the working volume of reactor 54. The liquid level or emulsion level 68 is preferably maintained at about fifty percent or one half of the volume of recycle reactor 54, which is generally the optimum liquid level. For example, using standard fifty-five gallon tank for recycle reactor 54, a preferred working volume of twenty seven and one half gallons is available. The liquid level 68 is maintained at the optimum level by sensing means, shown in figure 1 as liquid manometer 70 on reactor 54. The liquid content of the emulsion in reactor 54 is graduated, with the liquid content increasing towards the bottom portion of reactor 54. The position of manometer 70 is preferably towards the bottom of reactor 54, and is preferably at a position below the outlet for line 56 to recycle pump 58, in order to more accurately monitor the amount of liquid present, and thus liquid level 68, in reactor 54. Electronic control means in the form of a sensing circuit (not shown) are interfaced with manometer 70 and control valve 22, so that control valve 22 is responsive to manometer 70. When manometer 70 detects or senses a liquid level which deviates above or below the optimum level, control valve 22 correspondingly decreases or increases the liquid feed rate to correct the level. Control of the gas feed rate, as well as removal of gas from reactor through line 48, may also be used to control liquid level.

Centrifugal separator 66 receives a continuous flow of stable emulsion from line 64. The stable emulsion as received by centrifugal separator is preferably within the low pressure range of twelve to 15 psig, and pressure is monitored by gauge 72 in line 64. A final emulsion product with predetermined physical and chemical characteristics is centrifugally separated from the recycle emulsion by separator 66 and is continuously removed from the top of separator 66 via line 74 as a low pressure overflow stream. The remaining semi-emulsion is continuously removed from separator 66 as a higher pressure underflow stream, which exits separator 66 along line or path 76 where it is returned or recycled back to reactor 54, providing a shearing action to the contents of reactor 54 as the semi-emulsion impinges on the contents of reactor 54. An important feature of the centrifugal separating means is the ratio of underflow to overflow rates, which, in the preferred embodiment, is within the range of about two to one and about four to one. This underflow rate to
overflow rate ratio range can be obtained through modification of commercially available cyclones by changing inlet, overflow, and/or apex orifice sizes (not shown). Typical commercially available cyclones for liquid-solid separation generally have orifice sizes that provide an underflow/overflow ratio which is the reverse of that required for the present invention.

Thus, the shearing action provided by the semi-emulsion as it is continuously recycled back to reactor tank 54 from separator 66, produces the stable emulsion from the unstable dispersion. Variation of the recycle pump rate to reactor working volume ratio, and the underflow to overflow rate ratio of the centrifugal separating means, allows continuous generation of final emulsion products having tailored bubble size and gas content.

The final emulsion product from the overflow stream of separator 66 may contain excess liquid. Line 74 thus directs the final emulsion to liquid removal means, which preferably comprises a dewatering cyclone 78. Water or other liquid is centrifugally removed from the final emulsion in cyclone 78, with the excess liquid exiting cyclone 78 via line 80 and control valve 82. The excess liquid may be returned to reactor 54 through line 84 to increase or otherwise control the liquid level therein. The final emulsion is then discharged as overflow from cyclone 78 through line 86 and control valve 88, where it is directed elsewhere for flotation or other applications.

While the apparatus 10 comprising the invention has been described above with two preliminary bubble generating and attrition means, it should be readily understood that the invention may be used with a smaller or larger number of preliminary bubble generating means, or with no preliminary bubble generating means. The recycle action within reactor 54, caused by the impingement of the semi-emulsion on the contents of reactor 54, forms the stable gas-liquid emulsion from which the final emulsion product is separated, and controls the physical and chemical properties of the final emulsion product. The recycle action is controlled by the recycle pump rate/reactor working volume ratio and underflow/overflow rate ratio of the separator as described above. Thus, stable gas-liquid emulsions can be generated using the apparatus 10 without preliminary bubble generating means, by directing mixed gas and liquid from the supply means directly to reactor 54 rather than directing an unstable gas-liquid dispersion to 54 as described above. However, the volume of stable emulsion and final product emulsion produced by this approach is relatively small, and it is thus economically preferable to provide reactor 54 with unstable gas-liquid dispersion from preliminary bubble generating means, as related above. Providing a preliminary gas-liquid dispersion to reactor 54, rather than supplying gas and liquid directly thereto allows economical high
volume generation of final gas-liquid emulsion products with tailored characteristics.

The preliminary bubble generating and attrition means are preferably arranged in serial flow communication, so that unstable emulsions are produced in stages, with coarser unstable dispersions being converted to finer unstable dispersions, and with each subsequent stage dispersion having a finer bubble size than produced at the earlier stages. The preliminary bubble generating and attrition means, however, may be arranged in a parallel fashion, however, with two or more preliminary bubble generating means simultaneously providing a relatively coarse, unstable gas-liquid dispersion to reactor 54. The serial arrangement of preliminary bubble generating means, as shown in figure 1, is generally preferable to a parallel arrangement. It is also contemplated that several serial arrangements of preliminary bubble generating devices could be employed in parallel. For example, the invention can employ a first set of first and second bubble generating devices to generate and deliver an unstable dispersion to reactor tank 54 simultaneously with a second or additional sets of first and second bubble generating devices, which also deliver unstable dispersion to reactor 54, thus increasing the amount of unstable dispersion supplied to reactor 54 and allowing industrial scale volume outputs of final emulsion product.

In a working example of the invention as embodied in apparatus 10 described above, a stable air-water emulsion was produced in quantities suitable for flotation treatment of waste streams. Feed water, at the rate of seven and a half gpm, twenty psig, and 30° C, was supplied to apparatus 10. Fifty ppm of standard surfactant for stabilizing air-water emulsions, such as sodium dodecyl sulphate based surfactants like Dawn (TM) or Tergitol (TM), was added to and mixed with the feed water. Feed air was provided at a rate of one cfm at twenty five psig. A one inch by ten inch bead bed was employed for the first bubble grinder 38, and an eductor with a one inch diameter inlet was used for the second bubble grinder 46. A fifty five gallon reactor was used for recycle reactor 54, with a working volume of twenty five to thirty gallons at zero to two psig. A positive displacement recycle pump with a pump rate or capacity of fifty gpm was employed for recycle pump 58, and was operated at ten to twenty-five psig. A three inch cyclone with an underflow/overflow rate ratio of 2.13 and a pressure of thirteen psig was used for centrifugal separation means. A three inch dewatering cyclone was used for water removal, with a final emulsion product feed rate of seventeen gpm and an inlet pressure of five psig, providing dewatered final emulsion at fifteen gpm. Using the apparatus 10 with these aforementioned particular features, a white creamy lather with water like flow characteristics and a half life of six minutes was obtained. The air content was fifty percent, with an average bubble size of fifty microns, and a
bubble size range of five to one hundred microns. A production rate of fifty gallons per minute is possible with the particular details outlined above, which can treat waste streams of up to a thousand gpm. The air content with this arrangement can be varied within the range of twenty to sixty five percent as desired, with a bubble size range from two to two hundred microns.

The above example is but one of many possible arrangements of the apparatus 10, and many variations may be employed for producing different types of gas-liquid emulsions and/or higher production rates. As mentioned above, many possible arrangements of preliminary bubble generating and attrition means may be employed with the invention as well as the first and second stage bubble generating devises shown in figure 1.

Referring now to figure 2, there is shown an alternative embodiment 90 of the reactor and second bubble generator portion of the invention. In this embodiment, preliminary bubble generating and attrition means in the form of eductor 92 and static mixer 94 are included within the interior of the recycle reactor means, shown in figure 2 as recycle reactor 96. This arrangement provides a more compact arrangement of the invention than shown in figure 1. The arrangement of the eductor 92 and static mixer 94 as shown in figure 2 is particularly effective in forming air-water dispersions, which are subsequently converted to a stable air-water emulsion in reactor 96.

Generally, gas-liquid dispersion from an external preliminary bubble generating means (not shown) outside reactor 96 is directed along line 98 to eductor 92. Eductor 92 is mounted in impact mixer 94 as shown in figure 2, so that discharged dispersion 100 from eductor 92 impacts with the surface 102 of the gas-liquid dispersion contained in impact mixer 94, thereby providing bubble attrition. Dispersion is removed from impact mixer 94 and directed into reactor 96 by tube 104. Impact mixer 94 is preferably a sealed unit or container, with eductor 92 as the only inlet and tube 104 as the only outlet. Preferably, the lower end 106 of tube 104 is positioned beneath the surface 102 of the dispersion contained in impact mixer 94.

The liquid level or emulsion level 108 in reactor 96 is preferably maintained at about one half of the reactor volume, as related above in the description of the first embodiment and as shown generally in figure 2. Impact mixer 94 is preferably structured and configured so that its top surface 110 is generally level with the preferred liquid level 108. Tube 104 is preferably L-shaped as shown in figure 2, so that upper end 112 of tube 104 is generally horizontal. Liquid level 108 is monitored by liquid manometer 114 in the same manner as related above for the first embodiment of the invention. A control valve (not shown) on a liquid feed line (not shown) responsive to manometer 114 controls the liquid level 108 in reactor 96.
The contents of recycle reactor 96 are removed along line 116 by the action of recycle pump 118 and directed along line 120 to control valve 122, and along line 124 to separating means, shown here as a centrifugal separator 126. Pressure gage 128 allows monitoring of operating pressure. As in the first embodiment, a final emulsion product is removed from separator 126 as an overflow stream and directed along line 130 to means for removing excess liquid (not shown) and to a final destination. A semi-emulsion underflow stream 132 exits the lower end 134 of separator 126 and returns to reactor 96. Reactor 96 preferably includes an opening 136 adjacent reactor top 138, with the lower end or portion 134 of separator 126 protruding into reactor 96 through opening 136, so that the underflow stream 132 causes bubble shearing or attrition as it impinges with the gas-liquid emulsion contained in reactor 96. The lower end 134 of separator 126 should be positioned far enough from liquid level 108 of reactor 96 so that a suitable shearing action can occur. Preferably, the lower end 134 of separator 126 is positioned about one half way between liquid level 108 and reactor top 138.

Excess gas or air in reactor 96 may be removed via gas outlets 140, and directed to eductor 92 for recycling via line 142. Gas outlets 140 are positioned in recycle reactor 96 above the liquid level 108 so that gas-liquid emulsion does not enter outlets 140.

The configuration shown in figure 2 operates in generally the same manner as that related above for its counterpart shown in figure 1. As in the embodiment of figure 1, the ratio of the pumping capacity or rate of recycle pump 118 to the working volume of recycle reactor 96 is preferably within the range of between about two to one and about three to one, and the ratio of the rates of the underflow stream from separator 126 to the overflow stream from separator 126 is preferably within the range of between about two to one and about four to one. The primary difference between the embodiment shown in figure 2 is the inclusion of preliminary bubble generating means within the recycle reactor to provide a more compact arrangement. As with the first embodiment, several possible arrangements of preliminary bubble generating and attrition means may be employed with the invention, including a plurality of bubble generating means which are arranged in series and/or parallel. Alternatively, the apparatus 90 shown in figure 2 could be used without additional preliminary bubble generating means, with mixed liquid and gas supplied along line 98 to eductor 92 and impact mixer 94, rather than a gas liquid dispersion from another bubble generating device.

Referring now to figure 3, there is shown a flow diagram which generally outlines the steps of the method for continuous generation of gas-liquid emulsions in accordance with the present invention.
At step 200, a liquid and a gas supply are provided. A variety of gases and liquids are contemplated for use with the invention as related above, and may be provided by any suitable means commonly used in the art, such as the gas and liquid feed lines shown generally in figure 1. The liquid provided in this step generally includes at least one surfactant of the types related above, and may contain additional surfactants or other chemical additives, depending upon the type of gas-liquid emulsion to be produced and the ultimate application of the emulsion.

At step 210, an unstable gas-liquid dispersion is formed. Preferably, step 210 is carried out by forming a first stage dispersion from the gas and, liquid provided in step 200, using a first preliminary bubble attrition means for grinding or shearing bubbles, and the first stage dispersion is generally coarse, having a relatively large bubble size and relatively short half-life. The preliminary bubble attrition means employed is of the sort related above in the description of the apparatus 10 and apparatus 90. Step 210 also preferably includes forming a second stage unstable gas-liquid dispersion having a somewhat finer or smaller bubble size. The second stage unstable dispersion is formed from the first stage dispersion by a second preliminary bubble grinding means or device.

At step 220, the unstable gas-liquid dispersion is directed to a recycle reactor or tank wherein a stable emulsion is formed. As in the apparatus 10 and apparatus 90 related above, the recycle reactor preferably includes means for monitoring and controlling the liquid level within the reactor.

At step 230, the stable emulsion is removed from the recycle reactor by means of a recycle pump. Preferably, the recycle pump has a pump rate which has a ratio to a working volume of the recycle reactor within the range of between about two to one and about three to one.

At step 240, a final emulsion product with predetermined physical and chemical characteristics is separated from the stable emulsion by centrifugal separation means, and a semi-emulsion is returned or recycled to the recycle reactor.

Generally, the separation means is a cyclone type device which removes the final emulsion as a low pressure overflow stream from the cyclone and allows the semi-emulsion to exit or return to the recycle reactor as a pressurized underflow. Preferably, the underflow rate and overflow rate have a ratio which is in the range of between about two to one and about four to one. The semi-emulsion creates a shearing or attrition effect as it is recycled or returned to the recycle reactor. Thus, the formation of the stable emulsion of step 220 is due to the recycle action of the semi-emulsion from step 240. The physical and chemical characteristics of the final emulsion are tailored by varying the ratio of the recycle pump rate to the reactor working volume, and/or by varying the underflow/overflow rate ratio of the
separator, which in turn effect the recycling of the semi-emulsion. The final emulsion product may additionally be dewatered or otherwise have excess liquid removed in an optional step (not shown).

The steps comprising the method of the invention as outlined above and shown in figure 3 are generally carried out simultaneously and continuously, to provide continuous generation of a final emulsion suitable for use in treating waste streams or other industrial applications.

The apparatus and method of the present invention can continuously generate stable gas-liquid emulsions in quantities not previously obtainable. The present invention thus makes possible a number of applications which have not been possible in the past or have been possible only on very limited scales. Particularly, the invention has numerous environmental flotation applications, such as clarification of turbidity in power plant cooling waters, removal of organic and inorganic dirt particles from wash water from vehicles, roads, runways, and ships, removal of slimes and particles from mine waters, removal of waste particles from food processing streams such as potato plants, canneries, and meat processing plants, removal of asbestos fibers from taconite plant and asbestos processing plant waste streams, and removal of solids from laundry and paint shop wastes. Similarly, there are several flotation applications for the present invention which are possible with addition of reagents, adsorbents, flocculants, or other additives to the liquid stream. For example, the removal of various particles formed into flocs may be carried out by addition of alum, ferric chloride, clays, and other flocculants and polyelectrolytes. Hydrocarbon hydrates may be removed from water by salt addition to the liquid feed, allowing discharge or recycling of runoff waters from airports, railroads, truck and ship terminals, the floors of industrial plants, the slops from steam cleaning railroad tank cars, tanker compartments, tank trucks, and waste streams generally from petrochemical plants and facilities. The removal of finely dispersed or solubilized hydrocarbons, oils, and solvents, as well as metal ions, may also be removed from waste streams by flotation with suitable chemical additives in the liquid feed used in generating the gas-liquid emulsion.

Various separation processes may be carried out with the invention, including separation of fermentation products, reaction products, or precipitates from mother liquors or solutions, and separation of particles produced in pulverization processes. Consumable foam products may be prepared using the present invention, including frozen foams as food items, foamed fuel/oxidizer mixes for firing boilers and furnaces, fire-fighting foams for fighting shipboard, tank farm, or other combustible liquid fires, and foamed cleaning products for industrial or home applications. Froths and foams generated using the present invention
may also be used in pipeline transportation of viscous liquids or fine solids, as heat transfer media, construction materials, sound suppressing foams, etchants, and for removal of gas from liquids and supersaturated solutions.

Accordingly, it will be seen that the present invention provides a method and apparatus for continuous generation of stable gas-liquid emulsions, which operates at low pressures, which provides suitable outputs for large industrial applications, and which is simple, involves inexpensive equipment, and has minimal labor requirements and energy consumption. Although the description above contains many specificities, these should not be construed as limiting the scope of the invention but as merely providing illustrations of some of the presently preferred embodiments of this invention. Thus, the scope of the invention should be determined by the appended claims and their legal equivalents.
Claims

What is claimed is:

Claim 1 - An apparatus for generating gas-liquid emulsions, comprising:
(a) recycle reactor means for converting a coarse, unstable gas-liquid dispersion into a stable gas-liquid emulsion;
(b) centrifugal separating means for centrifugally separating and removing a final emulsion with predesigned physical and chemical characteristics from said stable gas-liquid emulsion, said centrifugal separating means returning a semi-emulsion to said recycle reactor means; and
(c) a recycle pump, said recycle pump receiving said stable emulsion from said recycle reactor means and directing said stable gas-liquid emulsion to said centrifugal separating means.

Claim 2 - An apparatus for generating gas-liquid emulsions as recited in claim 1, further comprising at least one preliminary bubble generating and attrition means for producing said unstable gas-liquid dispersion, said preliminary bubble generating and attrition means providing said unstable dispersion to said recycle reactor means.

Claim 3 - An apparatus for generating gas-liquid emulsions as recited in claim 1, wherein said recycle pump comprises a positive displacement pump, said recycle pump directing said stable gas-liquid emulsion from said recycle reactor means to said centrifugal separating means, said recycle pump having a pumping capacity which has a ratio to a working volume in said recycle reactor means of between about two to one and about three to one.

Claim 4 - An apparatus for generating gas-liquid emulsions as recited in claim 1, wherein said final emulsion is removed as an overflow stream from said stable gas-liquid emulsion by said centrifugal separating means, and said semi-emulsion is removed by said centrifugal separating means as an underflow stream, said underflow stream having a ratio to said overflow stream in the range of between about two to one and about four to one.

Claim 5 - An apparatus for generating gas-liquid emulsions as recited in claim 2, further comprising supply means for providing liquid and gas, said supply means including means for mixing said liquid and said gas, said supply means including means for adding chemical additives to said liquid, said supply means providing said liquid and said gas to said preliminary bubble generating means.

Claim 6 - An apparatus for generating gas-liquid emulsions as recited in claim 1, wherein said recycle reactor means includes means for controlling and monitoring a liquid level in said recycle reactor means.
Claim 7 - An apparatus for generating gas-liquid emulsions as recited in claim 1, further comprising means for removing excess liquid from said final emulsion.

Claim 8 - An apparatus for continuously generating gas-liquid emulsions, comprising:
(a) supply means for providing liquid and gas, said supply means including means for mixing said fluid and said gas;
(b) preliminary bubble generating and attrition means for producing an unstable gas-liquid dispersion from said gas and liquid provided by said supply means;
(c) recycle reactor means for converting said unstable gas-liquid dispersion from said preliminary bubble generating means into a stable gas-liquid emulsion, said recycle reactor means including a recycle pump; and
(d) centrifugal separating means for centrifugally separating and removing a final emulsion with designed physical and chemical characteristics from said stable emulsion, said centrifugal separating means returning a semi-emulsion to said recycle reactor means.

Claim 9 - An apparatus for continuously generating gas-liquid emulsions as recited in claim 8, wherein said recycle pump comprises a positive displacement pump, said recycle pump directing said stable gas-liquid emulsion from said recycle reactor means to said centrifugal separating means, said recycle pump having a pumping capacity which has a ratio to a working volume in said recycle reactor means of between about two to one and about three to one.

Claim 10 - An apparatus for continuously generating gas-liquid emulsions as recited in claim 8, wherein said final emulsion is removed as an overflow stream from said stable gas-liquid emulsion by said centrifugal separating means, and said semi-emulsion is removed from said stable gas-liquid emulsion by said centrifugal separating means as an underflow stream, said underflow stream having a ratio to said overflow stream in the range of between about two to one and about four to one.

Claim 11 - An apparatus for continuously generating gas-liquid emulsions as recited in claim 8, further comprising second preliminary bubble generation and attrition means in sequential flow communication with said first preliminary bubble generating and attrition means.

Claim 12 - An apparatus for continuously generating gas-liquid emulsions as recited in claim 8, wherein said preliminary bubble generating and attrition means comprises a first bubble generator and a second bubble generator, said first bubble generator receiving said liquid and said gas from said supply means and producing therefrom a first stage unstable, coarse, gas-liquid dispersion, said second
bubble generator receiving said first stage dispersion from said first bubble generator and producing therefrom a second stage, finer, unstable gas-liquid dispersion, said recycle reactor means receiving said second stage dispersion from said second bubble generator.

Claim 13 - An apparatus for continuously generating gas-liquid emulsions as recited in claim 8, wherein said recycle reactor means includes means for monitoring and controlling a liquid level in said recycle reactor means.

Claim 14 - An apparatus for continuously generating gas-liquid emulsions as recited in claim 8, wherein said supply means further comprises means for adding chemical additives to said liquid.

Claim 15 - An apparatus for continuously generating gas-liquid emulsions as recited in claim 8, further comprising means for removing excess liquid from said final emulsion.

Claim 16 - An apparatus for continuous generation of gas-liquid emulsions, comprising:

(a) supply means for providing liquid and gas, said supply means including means for mixing said liquid and said gas, said supply means including means for adding chemicals to said liquid;

(b) a first preliminary bubble generating and attrition means for producing a coarse, unstable, first stage gas-liquid dispersion, said first bubble generating means receiving said liquid and said gas from said supply means;

(c) a second preliminary bubble generating attrition means for producing a second stage, finer, unstable gas-liquid dispersion said from said first stage gas-liquid dispersion, said second bubble generating means receiving said first stage dispersion from said first bubble attrition means;

(d) recycle reactor means for converting said second stage gas-liquid dispersion into a stable gas-liquid emulsion, said reactor means activated by a recycle pump, said recycle reactor means including means for monitoring and controlling a liquid level in said recycle reactor means, said recycle reactor means receiving said second stage gas-liquid dispersion from said second bubble generating means; and

(e) centrifugal separating means for centrifugally separating and removing a final emulsion from said stable gas-liquid emulsion, said centrifugal separating means receiving said stable gas-liquid emulsion from said recycle pump and recycle reactor means, said centrifugal separating means removing said final emulsion as an overflow stream from said stable gas-liquid emulsion, said centrifugal separating means returning a semi-emulsion to said recycle reactor as an underflow stream.
Claim 17 - An apparatus for continuously generating gas-liquid emulsions as recited in claim 16, wherein said recycle pump is a positive displacement pump, said recycle pump having a pump capacity with a ratio to a working volume in said reactor means in the range of between about two to one and about three to one.

Claim 18 - An apparatus for continuously generating gas-liquid emulsions as recited in claim 17, wherein said underflow stream has a flow rate which has a ratio in the range of between about two to one and about four to one to a flow rate for said overflow stream.

Claim 19 - An apparatus for continuously generating gas-liquid emulsions as recited in claim 18, further comprising means for removing excess liquid from said final emulsion.

Claim 20 - A method for generating gas-liquid emulsions, comprising the steps of:

(a) providing a supply of specific liquid and gas, said liquid including at least one surfactant.
(b) forming an unstable, gas-liquid dispersion from said liquid and said gas;
(c) directing said unstable dispersion to a recycle reactor and forming a stable gas-liquid emulsion therein from said unstable dispersion;
(d) removing said stable emulsion from said recycle reactor by a recycle pump; and
(e) separating a final emulsion with predetermined physical and chemical characteristics from said stable emulsion and returning a semi-emulsion to said recycle reactor.

Claim 21 - A method for generating gas-liquid emulsions as recited in claim 20, wherein said removing step (d) is carried out by a positive displacement recycle pump having a recycle pumping capacity with a ratio to a working volume in said recycle reactor in the range of between about two to one and about three to one.

Claim 22 - A method for generating gas-liquid emulsions as recited in claim 20, wherein said separating step (e) is carried out by centrifugal separating means for centrifugally separating said final emulsion from said stable emulsion, said final emulsion separated from said stable emulsion as an overflow stream by said centrifugal separating means, said semi-emulsion returned to said reactor as an underflow stream by said centrifugal separating means, said underflow stream and said overflow stream having flow rates with a ratio in the range of between about two to one and about four to one.

Claim 23 - A method for continuously generating gas-liquid emulsions as recited in claim 20, wherein said forming step (b) is carried out by at least one
preliminary bubble generating and attrition means for producing said unstable gas-liquid dispersion.

Claim 24 - A method for continuously generating gas-liquid emulsions as recited in claim 23, wherein said forming step (b) further comprises the steps of:

(a) forming a first stage coarse, unstable dispersion from said liquid and said gas by a first preliminary bubble generating and attrition device; and

(b) forming a second stage, finer, unstable dispersion from said first stage dispersion by a second preliminary bubble generating and attrition device.

Claim 25 - A method for continuously generating gas-liquid emulsions as recited in claim 20, further comprising the step of monitoring and controlling the liquid level in said recycle reactor.

Claim 26 - A method for continuously generating gas-liquid emulsions as recited in claim 20, further comprising the step of removing liquid from said final emulsion.

Claim 27 - A method for continuously generating gas-liquid emulsions, comprising the steps of:

(a) providing a supply of liquid and gas, said liquid including at least one surfactant;

(b) forming a first stage, coarse, unstable gas-liquid dispersion from said liquid and said gas with a first preliminary bubble generating and attrition means for producing said first stage gas-liquid dispersion;

(c) forming a second stage, finer, unstable dispersion from said first stage gas-liquid dispersion with a second preliminary bubble generating and attrition means for producing said second stage dispersion;

(d) directing said second stage dispersion to a recycle reactor and forming a stable gas-liquid emulsion therein, said recycle reactor including means for monitoring and controlling liquid levels inside said reactor.

(e) removing said stable gas-liquid emulsion from said recycle reactor with a positive displacement recycle pump, said recycle pump having a recycle pump rate with a ratio to a working volume in said reactor of between about two to one and about three to one; and

(f) separating a final emulsion with predetermined physical and chemical characteristics from said stable gas-liquid emulsion by centrifugal separating means for removing said final emulsion from said stable gas-liquid emulsion, said final emulsion separated from said recycle emulsion as an overflow stream by said centrifugal separating means, said centrifugal separating means returning a semi-emulsion to said recycle reactor as an underflow stream, said underflow stream and said overflow stream having flow rates with a ratio in the range of between about two to one and about four to one.
Claim 28 - A method for continuously generating gas-liquid emulsions as recited in claim 27, wherein said forming said stable emulsion in step (d) is carried out by said returning of said semi-emulsion to said reactor in step (f).
200 PROVIDE LIQUID AND GAS SUPPLY

210 FORM AN UNSTABLE GAS–LIQUID DISPERSION

220 DIRECT UNSTABLE DISPERSION TO RECYCLE REACTOR MEANS AND FORM A STABLE EMULSION THEREIN

230 REMOVE STABLE EMULSION FROM RECYCLE REACTOR MEANS

240 SEPARATE A FINAL EMULSION WITH PREDETERMINED PHYSICAL AND CHEMICAL CHARACTERISTICS FROM THE STABLE EMULSION AND RETURN A SEMI–EMULSION TO RECYCLE REACTOR MEANS

Figure 3
INTERNATIONAL SEARCH REPORT

A. CLASSIFICATION OF SUBJECT MATTER
IPC(6) : B01J 13/00; B01D 45/12, 47/00; B04C 5/30
US CL : 252/307, 314; 55/459.1; 95/150, 154
According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED
Minimum documentation searched (classification system followed by classification symbols)
U.S. : 252/307, 314; 55/459.1; 95/150, 154; 261/Dig.1

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

<table>
<thead>
<tr>
<th>Category</th>
<th>Citation of document, with indication, where appropriate, of the relevant passages</th>
<th>Relevant to claim No.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Y</td>
<td>US, A, 4,584,002 (COX ET AL.) 22 April 1986, see entire document and in particular column 1, lines 17-18.</td>
<td>1-28</td>
</tr>
<tr>
<td>Y</td>
<td>US, A, 4,780,243 (EDGLEY ET AL.) 25 October 1988, see entire document and in particular column 10, lines 28-31.</td>
<td>1-28</td>
</tr>
</tbody>
</table>

Date of the actual completion of the international search
26 JUNE 1996

Date of mailing of the international search report
05 JUL 1996

Name and mailing address of the ISA/US
Commissioner of Patents and Trademarks
Box PCT
Washington, D.C. 20231
Facsimile No. (703) 305-3230

Authorized officer
DANIEL S. METZMAIER
Telephone No. (703) 308-1235

Form PCT/ISA/210 (second sheet)(July 1992)*