PROCESS FOR HYDROLYSIS OF FATS AND OILS

Fig. 1

Fig. 2

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Another object of the invention is to provide a process and apparatus of the above character in which greatly improved reaction rates are obtained.

Another object of the invention is to provide a process and apparatus of the above character in which excellent reaction rates in the liquid phase have been obtained both with a great excess of water over that required for stoichiometry and also when no appreciable excess water is present.

Another object of the invention is to provide apparatus of the above character which is relatively simple and which can be constructed relatively economically.

Additional objects and features of the invention will appear from the following description in which the preferred embodiments are set forth in detail in conjunction with the accompanying drawing.

Referring to the drawings:

FIGURE 1 is a side elevational diagrammatic view illustrating apparatus for carrying out my process.

FIGURE 2 is a flow diagram illustrating my process.

The present invention involves a continuous hydrolysis operation in which the fat or oil to be hydrolyzed is introduced into a reactor in either solid or liquid form. The solid or liquid fat is then heated to a temperature ranging from 150° to 350° C. so that it is in a liquid phase. The liquid phase is then perturbed with a gaseous phase. In a preferred embodiment, this gaseous phase can be in the form of superheated steam. Alternatively, the water can be introduced in an aqueous phase and then transformed into the gaseous phase by the application of heat in the reactor. Also, alternatively, an additional inert gas, such as nitrogen, can be utilized in conjunction with a liquid aqueous phase. The gaseous phase, while passing through the reactor, perturbs the liquid phase or phases under conditions of my invention and thereby induces extreme turbulence in the liquid phase which is also passing through the tubular reactor to provide a greatly increased rate of molecular collisions within the liquid phase and also greatly increase the interfacial area between the liquid and gaseous phases, allowing reactions to proceed rapidly. This process can be carried out at relatively low pressures and is preferably carried out at or near atmospheric pressure or “in vacuo.” The liquid fat phase is maintained at a temperature ranging from 150° to 350° C. so that the reaction, e.g., hydrolysis, occurs at a very rapid rate. At or near atmospheric pressure, the reaction product, e.g., the fatty acid and glycerine, is volatilized into the vapor phase from which it can be readily isolated in purified form.

The invention can be better understood by reference to FIGURES 1 and 2. The apparatus shown in FIGURE 1 consists of a reactor 10 which is in the form of a relatively long tube 11 of a suitable material such as stainless steel. The tube 11 is covered with a heating jacket 12 of a conventional type and which is heated by suitable means such as superheated steam, hot oil or “Dowtherm,” or electrical heating elements so that a heated reaction zone is formed in the tube.

Suitable feeding means 16, such as a T, is provided on the inlet end of the reactor 10. A continuous flow of fat at a controlled rate is supplied through a pipe 17 to the T 16 and to the reactor 10. A continuous flow of steam at a controlled rate is supplied through a pipe 18 to the T 16 and to the reactor 10. Alternatively, water and a gas may be supplied to the pipe 18.

The outlet or effluent end of the reactor 10 is connected to a cyclone separator 21 of a conventional type which separates the vapor phase from the liquid phase. The vapor phase, as hereinafter described, contains the products of the hydrolysis, i.e., fatty acids and glycerine of distillation quality, which are fed by a pipe 22 into a
The glycerine and the fatty acids are separated from the steam in the recovery unit 23 as indicated and the steam is recirculated through a pipe 24 into the reactor 10. The unreacted fat or partially hydrolyzed fat in the residue of the separator 21 is recirculated through a pipe 26 and fed into the reactor 10 for reuse.

When using apparatus of FIGURE 1 to carry out the present invention, fat is supplied in a suitable form at a continuous and controlled rate to the pipe 17. The fat can be in the form of a solid if it can be fed at a uniform and controlled rate. However, in order to facilitate handling of the fat, it normally is desirable to melt the fat in a suitable manner such as in a kettle. Then, if desired, the fat can also be preheated in a suitable manner such as by running the molten fat through a coil immersed in hot oil. If such preheating is utilized, it is generally preferable not to heat the fat above 220° C., and preferably approximately to 200° C. The molten fat thus can be pumped through the preheater and fed to the reactor 10 through the pipe 17 at a continuous and controlled rate so that it is introduced into the reactor 11 in a liquid phase. The reactor 10 is maintained at a suitable temperature and preferably at a temperature ranging from 150° to 350° C.

The liquid phase which is flowing through the reactor is perturbed by a gas phase to cause extreme turbulence within the liquid phase.

By creating this turbulence in the liquid phase, a great improvement occurs in the mass transfer rates which makes a correspondingly great improvement in the hydrolysis rate. This great improvement in mass transfer rates is caused by an increased rate of molecular collisions within the liquid phase and also because of a great increase in the interfacial area between the liquid and gaseous phases.

There is a relationship between the mass transfer rates and the rate of flow of the liquid and the gas phases in the reactor. As is well known to those skilled in the art, when a liquid moves at a relatively slow velocity, the liquid tends to follow stream lines with little radial interchange of the molecules at once localized with respect to the molecules at another locale. As the speed of the liquid phase is increased, turbulence begins to develop in the liquid phase and becomes increasingly great as the speed increases. However, by the introduction of a gas phase along with the liquid phase, it is possible to perturb the stream lines of the liquid phase at a much lower liquid phase speed and to thereby increase the liquid phase under conditions where there would only be a streamlined flow if the liquid phase were flowing by itself. Thus, it can be seen that the introduction of the gaseous phase along with the liquid phase into the reactor serves two important functions, one of which is to create turbulence within the liquid phase, and the other of which is to greatly increase the interfacial area for reaction between the gas phase and the liquid phase.

In order to obtain optimum mass transfer rates, it is desirable that the flow conditions employed in the reactor be generally in the "slug" or "annular" region. These terms are defined in my article entitled, "Heat Transfer and Pressure Drop in Two-Phase Flow," published in the Chem. Eng. Prog. Symp. Series, 57, No. 32, 104-110 (1961). As pointed out in this article, two-phase heat transfer coefficients can be quantitatively expressed in terms of three regions which are termed "stratified," "slug" and "annular" and roughly in order of increasing proportions of gas to liquid. The "stratified" type of flow can be characterized by the liquid and gas phases moving as continuous layers through the reactor with and without surface wave motion. The "slug" flow conditions are characterized as in which the liquid component or phase moves in large slugs alternately with slugs of gas. The "annular" flow condition can be characterized as one in which the liquid phase moves as an annulus within the reactor and wherein the gas travels within the annulus.

These flow conditions are determined primarily by the actual liquid velocity relative to the reactor wall. However, these flow conditions are also influenced by the relative velocity of the gas and the liquid phases. Also, if the proportion of gas to liquid is increased sufficiently, atomization occurs.

From the foregoing, it can be stated that the preferred flow conditions for the accomplishment of a rapid reaction with random mass transfer are in the slug and annular regions. The greatest turbulence in the liquid phase occurs when the flow is in the slug region and particularly at the boundary between the slug and annular regions. In the annular flow region, partial atomization of the liquid occurs which results in a greater interfacial area between the liquid and gas phases. Thus, processes which are more dependent upon interfacial areas are preferably operated in the annular region. However, again, the flow conditions should be such that the fluid in the annular region is nearer the slug region because the drop dispersions are the least stable in this area with a consequent high frequency of coagulations and redispersions.

In carrying out my invention, the gas phase can take several forms. For example, as shown in FIGURES 1 and 2, it can be in the form of steam which is introduced at a continuous and controlled rate through the pipe 18 and into the reactor 10. The steam can be at any desired temperature. However, it has been found that it may be preferable to introduce the steam at approximately the same temperature at which the reactor is being operated. When such is the case, the steam can be preheated in a suitable device such as by passing the steam through a coil which is immersed in hot oil. The steam thus preheated is introduced as superheated steam into the reactor 11. The introduction of the steam perturbs the liquid phase in the manner described above. The reactor is continuously heated to continuously supply heat to the liquid and gas phases as indicated in step 31 in FIGURE 2 to maintain the liquid and gas phases at a temperature ranging from 150° to 350° C. so that hydrolysis will occur as indicated in step 32. Hydrolysis occurs at a very rapid rate because of the mass transfer hereinbefore described which occurs in the slug and annular regions of flow.

The hydrolysis is preferably carried out at or near atmospheric pressure because this greatly simplifies and reduces the cost of the apparatus for carrying out the process. It facilitates the volatilization of the fatty acids and glycerine into the vapor phase. However, if desired, the reactor can be operated under a vacuum as, for example, a vacuum down to 10 millimeters of mercury and a pressure up to 300 p.s.i. However, as hereinbefore explained, operating at the higher pressures may not be as desirable for certain purposes as operating at a near atmospheric pressure.

As is well known to those skilled in the art, when hydrolysis takes place within the reactor, water is required. When only steam is utilized as the gas phase, the water required is removed from the steam and the glycerine as well as some or all of the fatty acids are vaporized and commingling with the steam. When operating at or near atmospheric pressure, excellent hydrolyzation is obtained even though the amount of water in the gaseous phase, i.e., steam, is not much greater than that required stoichiometrically (3 mols of water for each mol of fat). The use of excess steam facilitates the volatilization of the fatty acids and glycerine. The excess of steam creates the same condition as a vacuum so that the fatty acids and glycerine pass into the vapor phase even though the temperature may be below their normal boiling temperatures at atmospheric pressure. When the reactor is operated at a pressure which is generally approximately 75 p.s.i. with a temperature below 175° C., the fatty acids and glycerines probably will be formed in a
liquid phase and, therefore, must be separated from the residue. When operating at such a pressure, it is desirable to decrease the amount of steam as much as possible to approach the stoichiometric quantity of water so as to obtain a high percentage of fatty acids and glycerine in the liquid phase as possible and to thereby reduce the cost of separating the fatty acids and glycerine from the water in the liquid phase.

Although a relatively large range of flow conditions can be utilized in my process in my apparatus, I have found that the liquid phase can have a linear velocity ranging from 10 to 15 feet per hour and that the gaseous phase can have a linear velocity of only a small amount per hour while still achieving flow in the sag or annular regions. With such velocities for the liquid and gas phases, the residence times within the reactor are relatively short although the residence times are also dependent upon the length of the reactor. Thus, I have found that residence times ranging from 5 to 30 seconds for the liquid phase and from 1 to 5 seconds for the gas phase give excellent results.

When the fatty acids and glycerine are formed in the vapor phase as pointed out above, the reactor is normally being operated at a temperature which is substantially above the liquefying temperature of steam and, therefore, the fatty acids and glycerine are essentially quite dry. Also, the concentration of glycerine is relatively high.

The effluent from the reactor 10 consisting of vaporized fatty acids, glycerine and steam and the liquid phase are separated in the cyclone separator 21 as indicated in step 33 shown in FIGURE 2. The liquid phase is removed in the separator 21 and is discharged as a residue which may contain unreacted or partially hydrolyzed fats. If this is the case, it may be desirable to recrystallize these unreacted fats through the reactor 10 through the pipe 26 as indicated in FIGURE 1. The separator 21 is operated at or near the temperature of the effluent from the reactor 11. However, because there is some heat loss in the separator, the cyclone separator 21 normally will be operating at a temperature which is below the temperature of the effluent.

The vaporized fatty acids, glycerine and the steam are removed from the separator through a pipe 22 and are supplied to a distillation unit 23 which again can take the form of a cyclone separator which is utilized for distilling the fatty acids and glycerine as shown in step 25. As is well known to those skilled in the art, this is readily possible because the glycerine and fatty acids have vapor pressures which are substantially below that of water. The distillation unit 23 can be operated at the temperature of the vapors which are supplied to it. However, this temperature is substantially above the liquefying temperature for steam, and hence this steam can be readily supplied without condensation to the inlet of the reactor through the pipe 24 where it again can be introduced into the reactor. If desired, as pointed out previously, the steam can be preheated to a superheated temperature before introduction into the reactor.

One of the important advantages of my process is that it is unnecessary to condense the steam because the steam can be utilized in the condition in which it is discharged from the distilling unit 23. This is particularly advantageous in that it eliminates the great amount of heat which is required for converting water back into steam. Comparatively speaking, the steam can be superheated to the desired temperature with a relatively small amount of heat, because of this substantially reduced heat requirement, this cost of performing the process and operating the apparatus is greatly reduced.

When the tubular reactor 10 is operated so that the glycerine and fatty acids are formed in a liquid phase and discharged with the residue from the separator, the residue is treated in a conventional manner. The fatty acids are solidified and removed. Thereafter, excess water is removed from the glycerine by evaporating the water.

When steam is used as the gas phase as explained above, an aqueous liquid phase is unnecessary. The mass transfer which occurs in my process, as explained above, causes hydrolysis to occur even though the steam and the fat are inherently immiscible. The water required for the hydrolysis comes from the steam. However, if desired, an aqueous liquid phase can be utilized in conjunction with a gas phase other than steam such as nitrogen. In this case, the gas phase will cause the desired turbulence in the aqueous liquid phase and the liquid fat phase to cause mass transfer to again occur and to thereby create a high rate of hydrolysis.

The hydrolysis referred to above normally is carried out with the use of a catalyst, such as sodium hydroxide, zinc oxide, potassium acetate, sulfuric acid, sulfonic acid and zinc chloride.

In order to obtain the greatest rates of hydrolysis in my process, the higher temperatures within the range specified are preferred. The use of high pressure is unnecessary. In fact, it is preferable to operate at atmospheric pressure or under a vacuum because operation in this manner tends to shift the equilibrium in favor of hydrolysis by vaporization of the fatty acid and glycerine at lower temperatures or to increase the percentage of vaporization of the fatty acids and glycerine at the same temperature. The important feature of my invention is that hydrolysis will take place at atmospheric pressure and in the absence of a condensed water phase. There is substantially no condensed phase water because the steam is superheated with the exception of any small amount of water which may be dissolved in the fat phase.

Examples of operation of my apparatus utilizing my process in which the reactor is of the type shown in FIGURE 1 and comprised of 3/4 inch IPS stainless steel pipe 45 feet in length are as follows:

**Example No. 1**

Animal fat (tallow) containing about 1% zinc oxide as the oleate was melted and metered into a fat preheating section where it was preheated to a temperature of approximately 100°C. The fat was then metered into the reactor at a continuous rate where it was contacted with a metered liquid water. The fat was preheated in the reactor at the rate of 100 grams per minute and the water was introduced at a rate of 70 grams per minute. Approximately the first part of the reactor was used as a preheater and steam generator, whereas the last 20 feet of the reactor was operated at a temperature of approximately 160°C with a pressure ranging from 80 to 90 p.s.i.g. An unexpectedly high degree of hydrolysis occurred within the reactor. With a single pass through the reactor, the hydrolysis was 15 percent of the possible hydrolysis which theoretically could occur. This high degree of hydrolysis was greater by more than ten times that which should have been obtained in accordance with results calculated from rate constants in the literature.

**Example No. 2**

Four kilograms of commercial tallow was charged into a feed tank with zinc oleate and potassium acetate where it was melted. This fat mixture was pumped at the rate of 100 grams per minute into a preheat section and heated to 200°C and then metered into the reactor. Live steam, equivalent to 30 grams water per minute, was charged through a steam preheater and heated to a temperature of 200°C. This live steam was contacted to the preheated fat stream as the fat stream entered the reactor. The reactor was maintained at a temperature ranging from 200°C to 280°C. The effluent was discharged into a fat recovery condenser and the condensate was discharged to a second cyclone to recover the fatty acids and glycerine. The excess steam was condensed in an effluent condenser. On the first pass of the liquid
fat, hydrolysis was 16 percent complete. When the glycerized mixture from the fat cyclone was recycled, the total conversion rose to 70 percent with no apparent limitation on the degree of hydrolysis. Essentially pure distilled grade fatty acids were readily recovered from the fatty acid recovery system. No attempt was made to isolate the glycerine. The steam phase had a linear velocity of 180,000 feet per hour and the fat phase had a linear velocity of 3500 feet per hour. The residence time per pass for the fat was from 10 to 30 seconds and the residence time for the steam was from \( \frac{1}{2} \) to 1 second. Substantially all of the fatty acids were in the vapor phase. The reactor was operated at atmospheric pressure.

**Example No. III**

A single pass run was carried out in accordance with Example No. II but utilizing the steam equivalent to 15 grams of water per minute. The percent of hydrolysis was 16 percent.

In the foregoing Examples I, II and III, the linear velocity of the liquid phase and the linear velocity of the gas phase were within the limits hereinbefore set forth.

By comparison of Examples II and III, it can be seen that the hydrolysis can be carried out with a great excess of steam. As pointed out, this is advantageous in that it facilitates the formation of the fatty acids and glycerine in the vapor phase which subsequently facilitates separation of the glycerine and fatty acids in relatively pure form in a simple inexpensive distillation operation. Examples II and III also show that my process is not limited by liquid phase equilibrium considerations.

From the foregoing, it can be seen that there are a great number of "degrees of freedom" which can be utilized in practicing my invention in which a gaseous phase is introduced into the reaction mixture. Thus, pressure, temperature, gas composition, the proportion of gas to liquid, etc., can all be varied within parameters set forth above to accomplish the desired results. For example, volatile reaction products can be stripped out of a liquid reaction mixture in situ, thus favoring the forward reaction as in esterification without necessarily resorting to vacuum operation. Moreover, such a procedure often provides means of at least preliminary purification of the reaction products. Conversely, a volatile reactant can be maintained largely in the liquid phase with the use of pressure and sufficient added gas to create the desired turbulence.

Although I have shown and described the reactor as being in a horizontal position with horizontal flow in the reactor, it is readily apparent that, if desired, the reactor can be positioned vertically to provide vertical flow. With the horizontal orientation pointed out above, the gas velocity would be as fast or faster than the liquid velocity. With vertical orientation, with the gas and liquid streams moving downwardly, the gas may travel at a lower absolute velocity than the liquid because of the buoyant effect of the gas. If both of the streams are traveling upwardly, the gas velocity would normally move as fast or faster than the liquid.

Although I have described my process and apparatus primarily in conjunction with the hydrolysis of fats and oils, my process and apparatus has applications to other hydrolytic processes. For example, alkyl halides could be produced by hydrolyzation with my process and apparatus. Also, amyl alcohol could be produced by hydrolyzing amyl chloride in an alkali system. The preparation of certain phenols should also lend itself to my process. For example, tetrachlorophenol-1,2,4,5, which is insoluble in water, could be reacted by itself or with a little methanol in a methanolic caustic solution under pressure. My process and apparatus also should be usuable for the oxidation of hydrocarbons. In such a reaction, the steam could be utilized to remove the heat of the reaction and also to moderate the reaction. Thus, a number of oxidation reactions could easily be carried out with my process and apparatus under conditions of extreme turbulence within the reactor which is characteristic of my invention.

Also, it is possible to reverse the procedure described above and use my process and apparatus to make esters instead of hydrolyzing them. This can be readily accomplished because water, which is the reaction product in the production of an ester from an alcohol and an acid, would go into the vapor phase and, therefore, push the equilibrium farther over to the side of the ester. Thus, my process would lend itself to the production of esters commercially in a continuous process instead of by a batch method.

Although I have stressed the use of my process and apparatus for hydrolytic processes, both can be used for volatilization. For example, my process and apparatus can be utilized for the stripping and deodorization of animal and vegetable oils. In such a use, the oil is intimately contacted by the gas phase (e.g. steam) during the violent turbulence which occurs within the confined reaction zones so that odor bodies and small amounts of fatty acids are stripped from the oil phase and removed in the effluent vapor (e.g. steam) phase in the substantial absence of hydrolysis. The residence times again are very short and the apparatus is relatively low in cost.

All of the foregoing reactions and volatilizations can be readily accomplished with my process and apparatus because they all involve mass transfer reactions in a confined zone. They are also reactions and volatilizations which involve two or more phases and in which one of the phases is a gas phase. For example, in the tetrachlorobenzene to trichlorophenol reaction, the tetrachlorobenzene is insoluble in water. It is, therefore, insoluble in sodium hydroxide and even if the mixture is heated to 200° C., there is no reaction. However, if methanol is added, the alkali is soluble in methanol and the tetrachlorobenzene is soluble in methanol to provide a single phase. This single phase is used in present commercial practice. Hydrolysis occurs at 175° C. and trichlorophenol is obtained by hydrolysis of one of the chlorine atoms on the benzene. By use of my process and reactor, it should be possible to cause this reaction to occur between a water phase and a tetrachlorobenzene phase by use of extreme turbulence induced into the liquid phase by a gas phase even though the phases are relatively immiscible.

It is apparent from the foregoing that I have not only provided a new and improved process and apparatus for the hydrolysis of fats and oils which can be utilized to provide a continuous process that can be carried out at or near atmospheric pressure, but relatively high production is possible because residence times have been substantially reduced. Also, costs of the apparatus utilized in the process are substantially less because of the reduced pressure requirements. It is also apparent that my invention provides a new environment of extreme turbulence and offers as a new, unique, low cost method and process for carrying out many chemical reactions. I claim:

1. In a process for the hydrolysis of fats and oils, forming the fat into a substantially liquid phase having a linear velocity ranging from 10^3 to 10^6 feet per hour, contacting the liquid phase with a gaseous phase substantially without hydrolysis having a linear velocity ranging from 10^3 to 10^6 feet per hour to perturb the liquid phase and to thereby induce extreme turbulence in the liquid phase and to cause flow of the gas and liquid phases in the slug and annular regions, and heating the liquid phase while it is being contacted by the gas phase under very rapidly rising temperature, the liquid phase at the time the gas phase is so introduced having a substantially liquid phase at the time the gas phase is so introduced.

2. A process as in claim 1 wherein the contacting of the liquid phase with the gas phase takes place at a tem-
perature ranging from 150° to 350° C. and a pressure ranging from a negative pressure of 10 millimeters of mercury to 300 p.s.i.

3. A process as in claim 1 wherein the gas phase is steam and wherein the contacting of the steam with the liquid phase takes place at substantially atmospheric pressure, the quantity of steam being substantially greater than that required stoichiometrically for hydrolysis so that at least one of the products of hydrolysis are volatilized in the vapor phase.

4. In a process for the hydrolysis of fats and oil, introducing the fat continuously at a controlled rate as a liquid phase having a linear velocity ranging from 10^4 to 10^5 feet per hour into a reaction zone, introducing a gas phase at a continuous controlled rate having a linear velocity ranging from 10^4 to 10^5 feet per hour into the reaction zone to contact the liquid phase and to perturb the liquid phase to thereby induce in the liquid phase extreme turbulence and to cause flow of the liquid and gas phases in the slug and annular regions, and heating the liquid phase in the reaction zone to a temperature to cause relatively rapid hydrolysis of the fat in the liquid phase so that an effluent containing fatty acids and glycerine is produced.

5. In a process for the hydrolysis of fats and oils, introducing the fat as a liquid phase in a continuous controlled rate exceeding 10^4 feet per hour into a confined reaction zone, introducing a gas phase at a continuous and controlled rate exceeding 10^5 feet per hour into the reaction zone, the gaseous phase containing water for hydrolysis of the fat, contacting the liquid phase with the gas phase to induce extreme turbulence in the liquid phase and to cause flow of the liquid and gas phases in the slug and annular regions, maintaining the reaction zone at a temperature above 150° C. and below a pressure of 300 p.s.i. to cause hydrolysis of the fats to take place during the time that the liquid phase is being perturbed by the gas phase to cause at least one of the reaction products to be volatilized in vapor phase, removing the vapor phase and the gas, separating the vapor from the gas, and recirculating the gas through the reaction zone.

6. A process as in claim 5 wherein the gas phase is steam and wherein an excess amount of steam is introduced into the reaction zone beyond that required stoichiometrically to enhance the formation of the reaction product in the vapor phase.

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