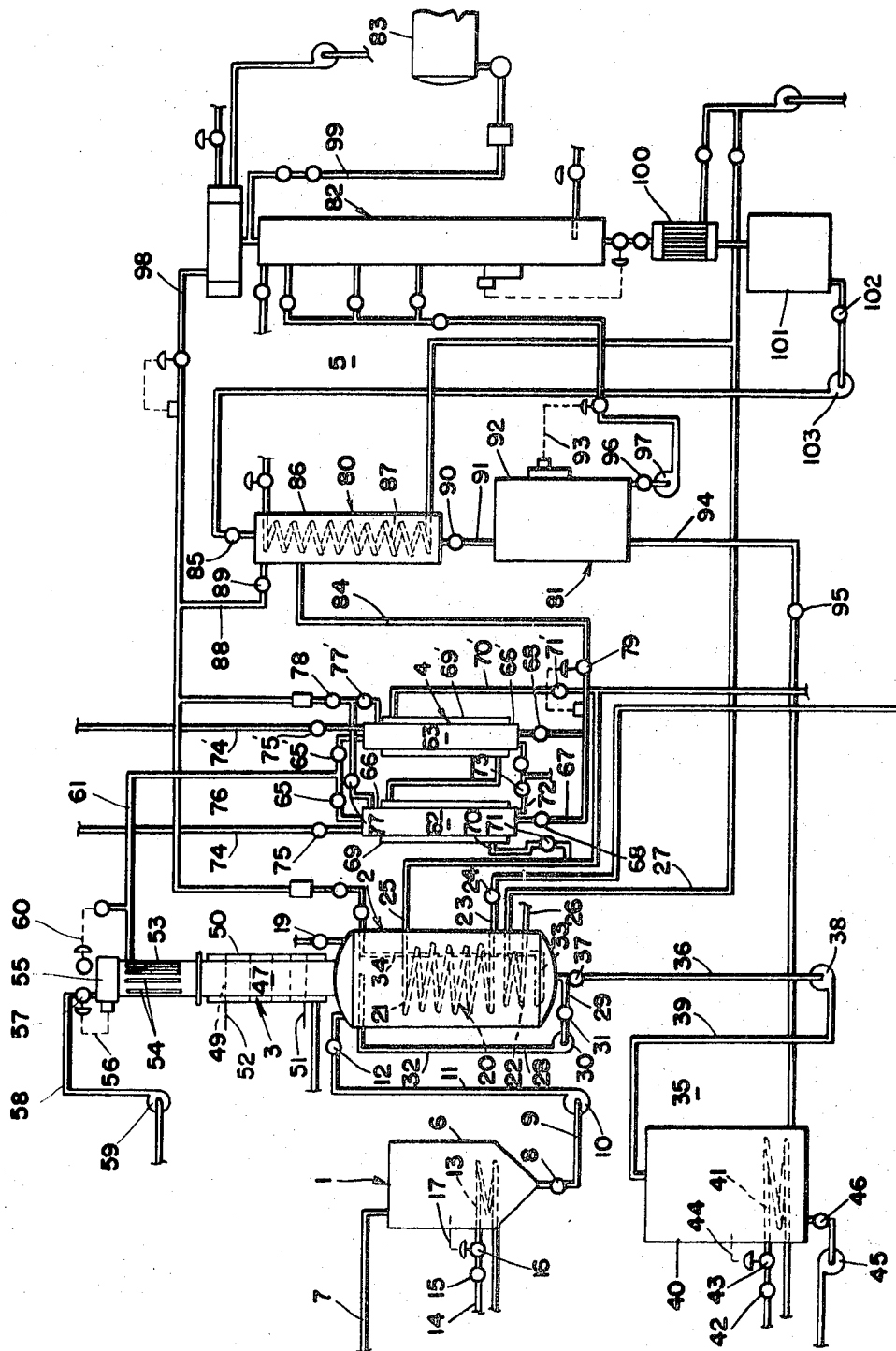


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METHOD FOR REACTING A MIXTURE OF CARBOXYLIC ACIDS  
WITH AMMONIA TO PROVIDE NITRILES  
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## METHOD FOR REACTING A MIXTURE OF CARBOXYLIC ACIDS WITH AMMONIA TO PROVIDE NITRILES

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9 Claims

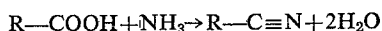
### ABSTRACT OF THE DISCLOSURE

A method of reacting a mixture of carboxylic acids which have varying boiling points with ammonia to provide nitriles. In the method, the mixture of carboxylic acids is reacted with ammonia in a liquid phase at a temperature above the boiling point of some of the carboxylic acids. The vapors from the liquid phase reaction are fractionated into a vapor containing ammonia and lower boiling carboxylic acids and a liquid containing higher boiling carboxylic acids and nitriles. The liquid from the fractionating step is returned to the liquid phase reaction as reflux. The vapor from the fractionating step is mixed with gaseous ammonia and is further reacted to provide nitriles.

The present invention relates generally to the preparation of nitriles, and more particularly, it relates to a method and apparatus for manufacturing nitriles by effecting reaction in the liquid phase and in the vapor phase.

The conversion of carboxylic acids to nitriles by reaction with ammonia has long been known. It is also known to effect this reaction in the liquid phase, particularly with the higher boiling fatty acids. It is further known to react ammonia with carboxylic acids in the vapor phase, and particularly with the use of carboxylic acids having lower boiling temperatures.

An over-all reaction which is well-known can be written as follows:



In the foregoing formula, R is a saturated or unsaturated straight or branched chain hydrocarbon radical which may also include an aromatic side chain.

Carboxylic acids for the reaction are derived from various sources, both natural and synthetic. Those from natural sources are produced by saponification or hydrolysis of triglyceride oils or acid oils by well-known procedures. The triglyceride or acid oils generally used are coconut palm kernel oil, cottonseed oil, soybean oil, groundnut (peanut) oil, tallow, marine oils, and tall oil. The synthetic carboxylic acids are derived from petroleum or hydrocarbons by known methods. Some of these oils contain fatty acid residues having widely varying chain lengths and one such oil, which is well-known, is coconut oil. The oils having widely varying chain length residues of fatty acid contain components having widely varying boiling points so that it is difficult to effect nitrilation under one set of conditions of reaction.

Of course, it is possible to fractionate or separate the carboxylic acids one from the other in the feed stock to provide a material which primarily comprises acids having closely proximate boiling points. However, this involves additional cost, loss of yield and various difficulties in manufacturing operations. In many instances, it is not necessary to separate the carboxylic acids to provide the desired nitrile and it would be desirable to effect nitrilation on fatty acid feed stocks obtained from a fat splitter or on a wide cut of synthetic acids obtained from

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petroleum. It would also be desirable to effect such a reaction to provide high yield and quality, and this can be done through the establishment of reaction in the liquid phase and in the gaseous phase.

In accord with this invention, apparatus and methods have been discovered for effecting nitrilation of carboxylic acids having varying boiling points. Such apparatus and methods provide nitriles of high quality in unusually high yield.

A principal object of this invention therefore is the provision of improved preparation of nitriles and to manufacture nitriles through reaction in the liquid phase and in the vapor phase.

A more particular object of this invention is the provision of an improved method and apparatus for preparing nitriles from carboxylic acids and particularly from carboxylic acids having varying boiling points.

A further object of this invention is the provision of an improved method and apparatus for manufacturing nitriles from carboxylic acid mixtures by effecting reaction in the liquid phase and in the vapor phase.

An additional object of the invention is to provide a method and apparatus for reacting a mixture of carboxylic acids with ammonia to provide nitriles of high quality in high yield.

The accomplishment of these objects of the invention will become apparent by reference to the description and accompanying drawing.

The drawing is a schematic representation of apparatus in accord with the invention.

Before describing the method of the invention, the drawing will be described in some detail so that the method can be more clearly understood. The apparatus shown in the drawings generally comprises a feed arrangement 1 which feeds into a liquid phase converter means 2. Disposed on top of the converter means 2 is a fractionating head 3 which is in communication with a vapor phase converter means 4. Associated with this apparatus is an ammonia system 5 which is adapted to provide ammonia to the liquid phase converter means 2 and the vapor phase converter means 4.

The feed arrangement 1 includes a tank 6 which can be used for measuring the feed stock which enters the liquid converter means 2. An inlet pipe 7 is provided for introducing the feed stock into the tank 6. The feed stock leaves the tank 6 through a valve 8 and pipe 9 and is introduced into the liquid phase converter means 2 by means of a centrifugal pump 10 which pumps through a pipe 11 and a valve 12 adapted to prevent reverse flow of material in the pipe 11.

In the tank 6, there is provided a heating coil 13 through which heating medium is introduced. The heating medium enters through line 14 and valve 15. The rate of flow of the heating medium is controlled by a valve 16 which is responsive to temperature of the feed stock in the tank 6. The response of this valve 16 to the temperature of the feed stock is schematically illustrated at 17.

In the liquid phase converter means 2, the feed stock is converted in liquid phase to nitrile. The liquid phase converter means comprises a pressure vessel 18 which is provided with a safety valve 19 for protecting the vessel against unusual pressure conditions. The pressure vessel 18 is fabricated from a suitable metal which will withstand the corrosion of materials reacted within the vessel 18.

Within the converter vessel 18 are heating and cooling means 20 which, in the illustrated embodiment, comprises a heating coil 21 and a cooling coil 22. The heating coil 21 is connected to a Dowtherm boiler (not shown) through line 23 and a control valve 24 so that the heating coil 21 is heated by the Dowtherm medium. The heating medium exits from the heat coil 21 through line 25.

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The cooling coil 22 is adapted to cool the contents of the converter vessel 18 when desired and connects to a source of coolant (not shown). The coolant enters through line 26 and exits through line 27.

In order to promote effective reaction of the materials within the converter vessel 18, the liquid phase converter means 2 further includes circulation means 28 for taking material from the vessel 18 at the bottom and returning it to the vessel at the top. The circulating means 28 includes a pipe 29 which communicates with the bottom of the pressure vessel 18 and with a pump 30 through a valve 31. The pump 30 returns the material to the converter vessel 18 through a leg 32 which enters the top of the vessel 18 and discharges the material therein.

The pressure vessel 18 may also be provided with agitator means but, in the illustrated embodiment, such means are not employed and are not shown in the drawing.

The liquid phase converter means 2 further includes an ammonia distributor 33 which connects to the ammonia system 5 through pipe 34. The distributor 33 is located at the bottom of the converter vessel 18 and sparges anhydrous ammonia into the materials contained within the converter vessel 18.

At the end of the reaction, the contents of the converter vessel 18 are discharged into storage means 35. The storage means includes a pipe 36 which connects to the bottom of the converter vessel 18 through valve 37. The pipe 36 connects to a pump 38 which pumps the reacted material through pipe 39 into a storage tank 40. The storage tank is provided with a heating coil 41 which communicates with a source of heat (not shown) through a valve 42. The rate of flow of the heating medium in the coil 41 is controlled by valve 43 which is responsive to the temperature in the storage tank 40 through means illustrated schematically at 44. The contents of the storage tank 40 may be pumped out by means of a pump 45 which connects to the bottom of the tank through valve 46.

The liquid phase converter means 2 communicates with the fractionating head 3 which extends vertically upwardly from the top of the converter vessel 18. The fractionating head 3 comprises a plate column 47 on which is disposed a condenser 48. The fractionating head 3 is quite important to the practice of the invention and functions to provide resolution of fatty acids, nitriles, water vapor and ammonia, as well as to effect a sharp separation between lower boiling and higher boiling materials.

The plate column 47 includes a series of vertically spaced trays 49 which are located within the column. These trays 49 are particularly effective to permit separation of the lower boiling carboxylic acids from the higher nitriles. The plate column 47 is provided with a heating jacket 50 which is important to prevent condensation of steam to liquid water within the column. The presence of liquid water in the column causes excessive foaming and loss of column fractionating efficiency. Steam is introduced into the jacket through line 51 and the spent steam discharges from the jacket through line 52.

The condenser 48 which is positioned on top of the plate column 47 is controlled within a relatively narrow temperature range and serves to minimize the loss of carboxylic acid. The temperature of this condenser will be chosen for the purpose of minimizing such loss and will be adjusted depending upon the particular feed stock which is introduced into the apparatus. The condenser 48 comprises an outer shell 53 within which are disposed condenser tubes 54. The condenser tubes 54 communicate with a header 55 which contains a coolant such as water. In order to provide relatively sharp control of temperature, the level of coolant within the header 55 is controlled by level control means 56 which operates a valve 57 in a supply line 58 through which coolant is pumped by the pump 59. The coolant may also be controlled by valve means 60 which is responsive to the temperature of the vapors leaving the condenser 48.

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The condenser 48 conducts vapors or gasses to the vapor phase converter means 4 through line 61. The vapor phase converter means comprises a pair of converters 62 and 63 which are adapted to convert the vapor phase materials to nitriles. These converters may be operated alternately, as will become apparent hereinafter.

The gases enter the vapor phase converter means 4 through line 61 and a valve 65. The vapor phase converter means comprises a tube 66 which is filled with bauxite ( $\text{Al}_2\text{O}_3$ ) for catalyzing the conversion to nitriles. The tube 66 connects at its outlet end to a line 67 through a valve 68.

For purposes of regenerating the bauxite in the tube 66, a heating jacket 69 is provided on the tube 66. This heating jacket is heated by means of a high heat medium, such as Dowtherm liquid, which enters the heating jacket through a pipe 70 in which there is a valve 71. Also for purposes of regenerating the bauxite, the tube 66 is provided at the lower end with an air inlet line 72 through which air enters through valve 73. The combustion gases are exhausted from the tube 66 through an exhaust line 74 in which is a valve 75. In regenerating the bauxite, air is admitted to the tube 66 through line 72 and valve 73. The jacket receives the heating medium, thereby heating the tube to combustion temperatures. Burning is effected within the tube 66 and combustion gases are exhausted through valve 75 and exhaust line 74. The various associated valves are operated to prevent combustion gases from entering the fractionating head 3, liquid phase converting means 4, and ammonia system 5.

The converter 63 is generally similar to converter 62 and includes like parts associated therewith and these parts have been similarly designated but have been differentiated by the symbol prime (') on the drawing.

For purposes of converting the low boiling carboxylic acids to nitriles, ammonia gas is introduced into the tube 66 through line 76 and valve 77. This ammonia line communicates with the ammonia system 5 through valve 78.

The discharge line 67 and 67' provides gases for recovery in the ammonia system 5 through a pressure control valve 79 which maintains a back pressure on the apparatus at a desired level to effect conversion of the low boiling carboxylic acids to nitriles in the apparatus. All of the gases from the apparatus exit through the pressure control valve 79 and enter the ammonia system 5.

The ammonia system is of commercially available design and will not be described in great detail. The ammonia system 5 is adapted to recover ammonia from the apparatus of the invention and provide make-up ammonia to the apparatus. As before indicated, the ammonia system provides ammonia for the liquid phase converter means 2 and the vapor phase converter means 4.

The ammonia system 5 comprises an absorber means 80, separating means 81 for recovering any organic materials which have come from the vapor phase converter 4 by entrainment or otherwise, and fractionating means 82. The ammonia system 5 further includes a make-up tank 83 for providing additional ammonia to the system.

The gases from the vapor phase converter means 4 enter the ammonia absorber 80 through line 84 which connects to the pressure control valve 79. The absorber 80 is operated under pressure and is provided with a weak ammonia liquor through a control valve 85. The liquor is sprayed into a tube 86 which contains a cooling coil 87. A by-pass line 88 enters the top of the tube 86 of the ammonia absorber 80 through a pressure control valve 89. The weak liquor, containing dissolved gases, discharges into the separating means 81 through a valve 90 and pipe 91.

The separating means 81 includes a tank 92 and a level control mechanism 93 for maintaining a level of liquid within the tank 92. Organic materials are recovered through pipe 94 and are pumped by the pump 95 to the

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storage tank 40. The separating means 81 discharges the weak liquor containing the dissolved gases from the absorber 80 through valve 96 and pump 97 to the fractionating means 82.

In the fractionating means 82, which comprises five theoretical plates, ammonia gas is recovered from the top of the fractionating means 82 for use in the liquid phase converter means 2 and the vapor phase converter means 4. The gas is fed through pipe 98 to these means 2 and 4. Make-up ammonia is fed from the make-up tank 83 through pipe 99 and into the line 98.

Liquor discharges from the bottom of the fractionating means through a cooler 100 into a tank 101. Liquor from the tank passes through valve 102 into pump 103 from which it is pumped to the top of the ammonia absorber 80.

Having described the apparatus of the invention, the process of the invention will be generally described and a specific example of the process will be set forth as practiced on the apparatus. In the process of the invention, any carboxylic acid can be employed which normally forms nitriles. The process of the invention, however, is particularly adapted for the manufacture of nitriles from fatty acids, which can either be saturated or unsaturated fatty acids. The fatty acid chain lengths may vary from 6 to 24 carbon atoms and the invention has particular application to mixtures of fatty acids having components with differing boiling points.

The carboxylic acid is introduced into a liquid phase converter and placed under pressure with heat. The fatty acid is mixed in the converter with a suitable catalyst and reacted therein with anhydrous ammonia. However, the reaction can be carried out without a catalyst. During reaction, the fatty acids are desirably recirculated in the converter to assure reaction of the ammonia and fatty acids.

During reaction, the mixture is refluxed into a fractionating heat comprising a column and condenser arrangement which effects resolution of fatty acids, nitriles, water and ammonia. The higher boiling nitriles and fatty acids are refluxed back into the converter and lower boiling nitriles and fatty acids leave the column and condenser in the fractionating head for further reaction in vapor phase.

The condenser in the fractionating head is operated to carefully control the separation of lower boiling and higher boiling fatty acids which pass through the column.

The lower boiling and unreacted fatty materials, in gaseous phase, with ammonia from the converter, pass into a vapor phase converter. In this connection, the mixture of gases, with added ammonia, is introduced into the vapor phase converter over a catalyst such as bauxite. The nitriles from the vapor phase converter are condensed and recovered.

The nitriles from the liquid phase converter are introduced into a tank and may be mixed with the condensed nitriles converted in vapor phase. Alternately, the nitrile products may be separately recovered and used.

The process of the invention, as before pointed out, effects the reaction of nitrile in liquid phase and in vapor phase but it is important that the fractions be separated between the phases in order to enjoy best results of the invention. Thus, it is important to reflux and separate the fatty materials and ammonia before introduction of gases into a vapor phase converter. This in accordance with the invention, is effected in the fractionating head, which also functions to prevent condensation of water and foaming during the course of the reaction.

Now referring to the drawings, distilled fatty acids obtained from the splitting of coconut oil are measured into the tank 6 in the amount of about 8,250 pounds. The distilled fatty acids are maintained at a temperature of about 65° C. in the tank 6 and are pumped into the converter vessel 18 by pump 10 through valve 8 and lines 9 and 11.

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In the converter vessel 18 is placed .05 percent zinc oxide and .05 percent bauxite, based upon the weight of fatty acids, which function as a catalyst. The converter vessel is then heated by introducing Dowtherm medium into the coil 21 at a temperature of about 360° C. The pressure in the converter vessel 18 should be at least 90 p.s.i.g. for converting coconut oil fatty acids but the range of pressure for conversion can be in the range of 25 p.s.i.g. to 200 p.s.i.g.

During heating, the circulation pump 30 is operated to circulate the fatty acids within the converter vessel 18. When the temperature of the fatty acids reaches about 95° C., anhydrous ammonia is injected into the converter vessel 18 at a maximum rate of 500 pounds per hour and into the vapor phase converter 4 at a maximum rate of 200 pounds per hour.

The system is then closed by operating the various valves, and the temperature of the fatty acids in the converter vessel 18 is raised to between about 260° C. to 335° C. in about two hours. Reaction within the converter vessel 18 causes water of reaction to be released, and excess ammonia, water of reaction, fatty acids and nitrile vapor ascend into the fractionating head 3 and enter the column 49 at the bottom of the fractionating head. The higher boiling fatty acid components are preferentially condensed and returned by reflux down the column 49. The walls of the column 47 are heated to a temperature in excess of the boiling temperature of water at the pressure in the column in order to prevent foaming due to condensation of steam to liquid water, which may result in formation of ammonia soap solutions within the column. This is important in the operation of the process of the invention to assure best operation.

The uncondensed fatty components, water vapor and ammonia pass to the condenser 53 to assure against any undue entrainment of the higher boiling fatty acids or nitriles into the vapor phase converter 4. In the particular example here involved, the condenser is operated so that the temperature of the tubes 54 is maintained at 165–166° C. plus or minus 2° C., and in any event is maintained above the condensation temperature of water under the pressure existing within the condenser. This is accomplished by control of the water in the header 55 and circulation through the condenser tubes 54. The effectiveness of the apparatus is in part determined by the close control of the condenser temperature so as to effect best separation.

The uncondensed fatty components, water and ammonia, enter the vapor phase converter 4 with an injected stream of ammonia through pipe 76. The mixed gases and vapors enter the vapor phase converter at about 90 p.s.i.g. The vapor and gases pass over the catalyst in the tube 66 and exhaust from the vapor phase converter through the control valve 79 which reduces the pressure to about 10 p.s.i.g. The gases and vapors pass through pipe 84 to the ammonia absorber 80 wherein the fatty material passes to the tank 92 and the fatty material is collected in the tank. The ammonia liquor in the tank is separated in the fractionating tower 82 to regenerate ammonia for the process.

One of the substantial advantages of the process of the invention is that through conversion of the low boiling carboxylic acids to nitriles, more effective recovery of ammonia is possible. Without this conversion in the vapor phase, foaming problems would arise in the ammonia system 5 which would greatly decrease fractionating efficiency. If the low boiling fatty acid materials were not converted to nitriles, it would be necessary to remove them or their complexes which would be difficult. In the described apparatus, the organic components in the vapors going to the ammonia system 5 are nitriles only, do not foam on heating, are substantially water insoluble, and are easily recovered by decantation with enhanced product yield. Thus, the apparatus and process of the

invention eliminates the need for pretreating feed stock, as by prefractionation to remove light ends.

The various features of the invention which are believed to be new are set forth in the following claims.

What is claimed is:

1. A batch process for reacting a charge of a mixture of carboxylic acids with ammonia to provide nitriles wherein the carboxylic acids have varying boiling points, comprising the steps of

(a) introducing into a liquid phase reaction zone a charge of carboxylic acid feed stock to be converted to nitrile, said feed stock being a mixture of nitrile-forming carboxylic acids having varying boiling points, so as to provide a liquid phase reaction mass in said liquid phase reaction zone.

(b) establishing in said liquid phase reaction zone a reaction pressure of between about 25 p.s.i.g. and about 200 p.s.i.g.,

(c) heating said liquid phase reaction mass to a liquid phase nitrile conversion reaction temperature above the boiling temperature at said reaction pressure of some of the carboxylic acids in said charge of carboxylic acid feed stock,

(d) introducing anhydrous ammonia into said heated liquid phase reaction mass and reacting said ammonia in the liquid phase with the carboxylic acids in said liquid phase reaction mass at said conditions of temperature and pressure to effect conversion of said liquid phase reaction mass to nitrile, and to provide reaction vapors comprising unreacted ammonia, water produced by the liquid phase nitrile conversion reaction, lower boiling nitriles and fatty acids vaporized from the liquid phase reaction mass,

(e) conducting said reaction vapors from the liquid phase reaction under pressure from the liquid phase reaction zone to a fractionating zone and thence to a condensing zone to which vapors passing through the fractionating zone are conducted,

(f) heating said fractionating zone to a fractionating zone temperature above the condensation temperature of water at the pressure in the fractionating zone,

(g) maintaining said condensing zone at a condensing zone temperature selected to minimize the loss of carboxylic acid from said liquid phase reaction zone, said condensing zone temperature being above the condensation temperature of water at the pressure existing in the condensing zone,

(h) fractionating said reaction vapors in said fractionating zone and condensing zone into a substantially water free fractionated liquid comprising higher boiling carboxylic acids and nitriles, and a fractionated vapor comprising ammonia, water, and lower boiling carboxylic acids and nitriles,

(i) returning said fractionated liquid to the liquid phase reaction mass as reflux for further reaction with ammonia in the liquid phase,

(j) mixing said fractionated vapor with gaseous ammonia,

(k) further reacting said fractionated vapor and gaseous ammonia in the vapor phase to convert unreacted lower boiling carboxylic acids in said fractionated vapor to nitrile,

(l) separately condensing and recovering the nitrile from said fractionated vapor which has been further reacted with ammonia in the vapor phase to provide a lower boiling nitrile product, and

(m) continuing said introduction of ammonia until the liquid phase reaction mass is substantially converted to nitrile to provide a finished batch of nitrile product in said liquid phase reaction zone.

2. A method in accordance with claim 1 wherein said carboxylic acids of said mixture are saturated or unsaturated fatty acids having carbon chain lengths of from 6 to 24.

3. A method in accordance with claim 2 wherein said further reaction in the vapor phase of said fractionated vapor from said fractionating step is in the presence of a bauxite catalyst.

4. A method in accordance with claim 2 wherein ammonia is recovered from said further-reacted fractionated vapor for recycle use in the process, and wherein a back pressure is maintained during said step of further reacting the fractionated vapor with ammonia in the vapor phase, which back pressure is reduced during said recovery of ammonia and said condensation and recovery of nitrile from the further-reacted fractionated vapor.

5. A method in accordance with claim 4 wherein said liquid phase reaction mass is circulated in said liquid phase reaction zone and wherein said introduction of ammonia into said liquid phase reaction mass is carried out by sparging into the bottom of said liquid phase reaction mass.

6. A method in accordance with claim 5 wherein said fractionating zone is heated to said fractionating zone temperature in excess of the condensation temperature of water at the pressure in the fractionating zone by means of steam heating.

7. A method in accordance with claim 5 wherein said carboxylic acids are distilled fatty acids obtained from the splitting of coconut oil, wherein said reaction pressure is at least 90 p.s.i.g., and wherein said reaction temperature is between about 260° C. and about 335° C.

8. A method in accordance with claim 7 wherein said reaction pressure is about 90 p.s.i.g., and wherein said condensing zone is maintained at 165–166° C. plus or minus 2° C.

9. A method in accordance with claim 8 wherein the liquid phase reaction is carried out in the presence of zinc oxide and bauxite as a catalyst, and wherein the maximum rate of introduction of anhydrous ammonia into said liquid phase reaction mass is about 500/8250 pounds per hour per pound of said feed stock, and wherein the maximum rate of addition of gaseous ammonia to said fractionating vapor is about 3/5 of the rate at which ammonia is introduced into said liquid phase reaction mass.

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