

Description

The present invention is directed to a process for producing anhydrides or nitriles from hydrocarbons, an oxygen-containing gas and ammonia in the presence of a suitable catalyst under conditions which achieve high efficiency and selectivity toward the desired product.

The production of anhydrides and nitriles by oxidation and ammoxidation, respectively, of an appropriate hydrocarbon in the presence of a suitable catalyst is well known. The production of acrylonitrile, for example, from a gaseous feed of propylene, ammonia and air is described by Bruce E. Gates et al in *Chemistry of Catalytic Processes*, McGraw-Hill (1979), pp. 380-384.

The feed is sent to an ammoxidation reactor where, in the presence of a suitable catalyst, acrylonitrile is produced along with lesser amounts of other nitrogen-containing compounds. The effluent from the ammoxidation reaction is quenched with water and the desired products are obtained in the liquid phase. The gas phase by-products, typically oxygen, carbon dioxide, carbon monoxide and unreacted hydrocarbon, are combined with natural gas and sent to a boiler for combustion as disclosed, for example, in US-A-3 591 620 and US-A-4 335 056. A typical ammoxidation process is illustrated in Figure 1 of the accompanying drawings.

US-A-4 609 502 discloses a cyclic process for producing acrylonitrile using propane as a starting material which is initially dehydrogenated catalytically in the presence of steam to form propylene. For ease of reference a process according to US-A-4 609 502 is shown in Figure 2 of the accompanying drawings.

The use of steam is in contrast to most conventional dehydrogenation processes which avoid steam primarily due to the costs involved. After ammoxidation, the effluent is quenched, the desired product removed, and the off-gases, including propylene and propane, are sent to an oxidation reactor to remove oxygen by selective reaction with hydrogen to form water vapour. The gas mixture exiting the selective oxidation reactor includes substantial amounts of methane, ethane and ethylene, which are by-products of dehydrogenation, and unreacted propylene in addition to carbon oxides. As an option, this gas mixture is split and a portion is sent to a separator which removes only carbon dioxide. A portion of the effluent from the separation is purged to remove light hydrocarbons. The nonpurged stream is mixed with the remainder of the oxidator effluent, fresh propane and steam, if necessary, and sent to the dehydrogenator where the propane is converted to propylene. Another option is to cool and liquefy the C₃ hydrocarbons therefrom and then vaporise them prior to recycle.

The aforementioned process suffers from several disadvantages. The amount of propane which is converted to propylene is only in the range of about 20 percent to 60 percent per pass, typically about 40 percent, and therefore, about 60 percent of the propane feed is recycled throughout the system. At conventional velocities, the presence of such large amounts of propane along with hydrogen and other gases can produce higher pressures in the ammoxidation reaction zone which can, in turn, result in decreased yields of acrylonitrile. This problem could be overcome by using a more efficient dehydrogenation catalyst, if such were commercially available. Also, there is no practical way in this scheme to selectively remove by-products of propane dehydrogenation, such as methane, ethane, ethylene and the like, thereby preventing their accumulation in the system. Providing a purge stream to remove these gases will also cause removal of some of the circulating propane and propylene. As the process is being carried on in a continuous manner, this loss of starting material causes a significant decrease in the yield of propylene. It is disclosed that propane and propylene are recovered from the purge stream prior to venting. Additional refrigeration is therefore necessary to liquefy the propane and propylene. This apparatus, as well as that required to vaporise them prior to recycle, significantly adds to the capital cost of the process.

Another disadvantage of the process shown in Figure 2 stems from the use of the selective oxidation reactor to treat the gaseous effluent from the quencher. The gases exiting the quencher are at ambient temperature and must be heated prior to introduction into the oxidation reactor in order to promote oxygen removal. Because there is a significant amount of oxygen in the quencher effluent, the heat of reaction generated in the oxidation reactor can result in excessive temperatures in the system. There are three options to alleviate this problem. First, the amount of oxygen entering the oxidation reactor can be reduced by other means. Second, multiple reactors can be utilised with a cooling means between each pair of reactors. Third, a portion of the effluent from the reactor is passed through a cooling means and recycled to the feed to reduce the internal temperature of the reactor. None of these measures is attractive from the viewpoint of cost and efficiency.

The oxidation reactor in the process shown in Figure 2 is operated with oxidation catalysts such as noble metals (e.g., platinum). Olefins and carbon monoxide, which are generated in the dehydrogenation reactor, are known to poison these catalysts, as disclosed in *Catalytic Processes and Proven Catalysts*, Charles L. Thomas, Academic Press (1970) pp. 118-119. Accordingly, multiple oxidation reactors must be

used to allow for frequent regeneration of the catalyst which represents yet another addition to production costs (US-4 609 502, column 4, lines 51-56).

Another recycle process, but for making maleic anhydride from n-butane and air, is disclosed in US-A-4 231 943. Maleic anhydride is separated from the gaseous effluent downstream of the oxidation reactor.

5 The resultant gaseous stream, free of maleic anhydride, is divided into two subsidiary streams. One subsidiary stream is returned directly to the oxidation reactor. The other subsidiary stream has n-butane separated therefrom and the resultant n-butane is recycled to the oxidation reactor. The use of air as a feedstock in combination with the absence of any selective separation stage to adjust the composition of the subsidiary stream that is fed back to the oxidation reactor results in a relatively inflexible process that
10 produces particularly low percentage conversions, particularly since there is an inherent limit on the amount of n-butane that can be recycled.

There is thus a need for an improved process which enables starting hydrocarbons to be recycled without substantial disadvantage.

According to the present invention there is provided a process for the production of nitriles and
15 anhydrides comprising:

(a) reacting in a reaction vessel under conditions which produce an effluent containing the nitrile or anhydride at low feed conversion and high selectivity:

either (i) if an anhydride is to be produced, a hydrocarbon and an oxygen-containing gas in the presence of an oxidation catalyst;

20 or (ii) if a nitrile is to be produced, a hydrocarbon, an oxygen-containing gas, and ammonia in the presence of an ammoxidation catalyst;

(b) quenching the effluent with a liquid to form a quenched liquid phase containing said nitrile or anhydride and a gaseous phase containing gaseous products including unreacted hydrocarbon;

(c) recovering said nitrile or anhydride from the liquid phase;

25 (d) introducing the gaseous phase into a selective separator to thereby remove a substantial portion of the unreacted reactant hydrocarbon; and

(e) recycling said unreacted reactant hydrocarbon to said reactor vessel, wherein the gaseous phase formed in step (b) contains from 30 to 95 percent by volume of flame suppressor.

30 Illustrative of products, and their respective starting materials, which can be advantageously produced by the method of this invention are acrylonitrile from propylene, methacrylonitrile from isobutylene, phthalonitrile or phthalic anhydride from o-xylene, maleic anhydride from n-butane and the like.

In contrast to the known process as referred to hereinabove, the process according to the present invention utilises a selective separator, preferably a pressure swing adsorption unit, which effectively
35 removes a substantial portion of the reactant hydrocarbon so that it can be recycled to the ammoxidation/oxidation reactor, thus providing a high overall yield and economy of operation. As utilised herein, the expression "a substantial portion" as it pertains to recycle of the reactant hydrocarbon, means at least 80 percent by volume where the oxygen-containing gas in the feed to the ammoxidation/oxidation reactor is air, at least 90 percent by volume where a mixture of equal parts of pure oxygen and air is
40 utilised as the oxygen-containing gas and at least 95 percent by volume where the oxygen-containing gas is pure oxygen. In each instance, these are minimum percents. Utilising pure oxygen as the oxygen-containing gas, for example, the amount of reactant hydrocarbon recycled is typically 97-99 percent by volume.

As the selective separator contemplated herein typically requires a pressurised feed, the process of the present invention provides an effective amount of a gaseous flame suppressor to minimise the flammability
45 potential at the introduction of the gaseous effluent from the quench tower into the means to raise the pressure thereof, e.g. a compressor. The gaseous flame suppressor of the present invention comprises a substantially unreactive hydrocarbon having from 1 to 5 carbon atoms, carbon dioxide and, where air or enriched air is utilised as the oxygen-containing gas in the feed to the ammoxidation/oxidation reactor, nitrogen. By "substantially unreactive" is meant that at least 95 percent by volume of the hydrocarbon
50 component of the gaseous flame suppressor will pass through the ammoxidation/oxidation reactor unchanged. The substantially unreactive hydrocarbon can be a saturated or unsaturated hydrocarbon with saturated being preferred.

The amount of the gaseous flame suppressor mixture in the subject cyclic process is controlled so that it will be maximised at the point or points in the system where it is of greatest advantage, i.e. the feed to
55 the pressure raising means. It will be appreciated that, when pure oxygen is utilised as the oxygen-containing gas in the feed to the ammoxidation/oxidation reactor, nitrogen will not be a component in the gaseous flame suppressor. In embodiments of the subject process to be described herein, each of the components of the gaseous flame suppressor mixture of the present invention will comprise a major portion

thereof.

Examples of specific substantially unreactive hydrocarbons utilised as a component of the subject gaseous flame suppressor and the reaction in which they are utilised include: isobutane for the production of maleic anhydride from n-butane; n-butane for the production of methacrylonitrile from iso-butylene; n-butane for the production of maleic anhydride from butylene and the like.

Onreacted hydrocarbon reactant, e.g. propylene, butylene and the like, while not a major portion of the gaseous flame suppressor, appears to enhance the flame suppressant capacity thereof. The amount of unreacted reactant hydrocarbon present in the gaseous flame suppressor mixture will depend on the percent per-pass conversion of the reactant hydrocarbon entering the oxidation/ammoxidation reactor which is converted to products. Those skilled in the art will appreciate that factors such as choice of catalyst, operating pressures and the like can be adjusted to have the ammoxidation/oxidation reactor operate at a desired conversion of the reactant hydrocarbon in the feed thereto. At lower operating conversions, e.g. 60 percent conversion, there will be a greater amount of unreacted reactant hydrocarbon circulating in the system. For example, using substantially pure oxygen in an ammoxidation/oxidation reactor operating at 80 percent conversion in accordance with the invention, there will be only about 10 to 15 percent unreacted reactant hydrocarbon in the quench tower effluent whereas, at 60 percent conversion, there will be a greater percent unreacted reactant hydrocarbon in the quench tower effluent. The composition of the gaseous flame suppressor will be adjusted accordingly.

The process of this invention is advantageous in that it provides the efficiency of recycle afforded by the process illustrated in FIG. 2, yet is free of the disadvantages inherent therein while, at the same time, being less complex. The advantages of the present invention are, in large measure, provided by the incorporation into the process of a selective separator which retains a substantial portion of the unreacted reactant hydrocarbon in the system. The gaseous flame suppressor of the subject process may be partially or totally recycled, depending on the operating conditions and feed to the system. In a preferred embodiment, the separator is a pressure swing adsorption unit.

Pressure swing adsorption (PSA) is a well known process for separating the components of a mixture of gases by virtue of the difference in the degree of adsorption among them on a particulate adsorbent retained in a stationary bed. Typically, two or more such beds are operated in a cyclic process comprising adsorption under relatively high pressure and desorption or bed regeneration under relatively low pressure or vacuum. The desired component or components may be obtained during either of these stages. The cycle may contain other steps in addition to the fundamental steps of adsorption and regeneration, and it is commonplace to have two or more adsorbent beds cycled 180° out of phase to assure a pseudo continuous flow of desired product. While it is conventional for the adsorption step of a PSA cycle to be carried out under pressure, it can run at ambient pressure with desorption under vacuum. It is the difference in pressure between the adsorption and desorption stages which is essential for operation of the system.

Processes according to the invention will now be described by way of example with reference to Figures 3 to 5 of the accompanying drawings,

FIG. 3 illustrating in a block diagram an embodiment of a process for producing acrylonitrile in accordance with the present invention utilising air or oxygen-enriched air as a feed to the ammoxidation reactor, a pressure swing adsorption unit as the separator wherein the flame suppressor contains a major portion of nitrogen.

FIG. 4 illustrating in a block diagram an embodiment of a process of producing acrylonitrile in accordance with this invention wherein the flame suppressor contains a major portion of propane; and

FIG. 5 illustrating in a block diagram an embodiment of a process of producing acrylonitrile in accordance with this invention wherein the flame suppressor contains a major portion of carbon dioxide.

Referring to FIG. 3 there is shown a process for producing acrylonitrile. A feed into a conventional ammoxidation reactor comprises propylene, ammonia and air or oxygen-enriched air. The oxygen-enriched air preferably contains from about 30 to about 80, most preferably from about 55 to 65, percent by volume of oxygen. Such mixtures may be produced by adjusting the capacity of a conventional oxygen-producing unit, e.g. a conventional PSA unit, or by mixing pure oxygen with air in the proper proportions. The use of oxygen-enriched air will produce a minimum concentration of nitrogen in the feed to the ammoxidation/oxidation reactor of from about 10 to 20 percent by volume of the feed into the reactor depending on the operating conversion of the reactor as discussed above. The minimum concentration of nitrogen in the reactor feed will result in the desired level of nitrogen in the feed to the compressor for the PSA unit separator as discussed hereafter.

The ammoxidation reactor utilised in the present process is conventional and may employ either a fixed or fluidised catalyst bed. A typical example of an ammoxidation reactor is disclosed in US-A-4 070 393 or in Gates et al., *ibid*, pp. 381-383. The reactor contains a conventional ammoxidation catalyst, such as bismuth-

molybdenum oxide, iron-antimony oxide, uranium-antimony oxide precipitated on silica and the like. Other suitable catalysts are disclosed, for example, in *Chemistry of Catalytic Processes*, Gates et al, McGraw Hill (1979) pp 349-350, and US-A-3 591 620. Other suitable catalysts are known to those skilled in the art.

The ammoxidation reaction is conducted at a temperature of from about 375° to 550°C, preferably from about 400° to 500°C, at low pressures, typically in the range of from about 108 to 308 kPa (about 2 to 30 psig), preferably from about 122 to 239 kPa (about 3 to 20 psig). The reactants are passed through the reactor at a relatively low velocity, typically in the range of from about 0.53 to 0.67 m/s (about 1.75 to 2.2 ft./sec). The ratio of oxygen to propylene in the feed is suitably in the range of 1.6:1 to 2.4:1 by volume. In the production of a nitrile, the ratio of ammonia to propylene in the feed is suitably in the range of 0.7 to 1.2:1 by volume.

The ammoxidation reaction results in the production of a major amount of acrylonitrile and minor amounts of acrolein, hydrogen cyanide, acetonitrile, and carbon oxides as well as unreacted oxygen, propylene and nitrogen. Commercially available propylene typically contains a small amount of propane unless additional costly processing is undertaken to remove it. This is advantageous since propane exerts a positive effect on the gaseous flame suppressor of the present process. In this embodiment, the propane is substantially recycled from the PSA unit. This gaseous mixture is quenched or scrubbed with a liquid, such as water, to dissolve the water soluble compounds for subsequent separation and recovery of acrylonitrile, acetonitrile and hydrogen cyanide.

The gas phase effluent from the quench tower is introduced into a PSA unit separator wherein unreacted propylene is separated from the other gases in the mixture. Although the adsorption stage of the PSA unit can be at ambient pressure, it is preferred to pass the quench tower gaseous effluent through a compressor or other suitable means to increase the pressure thereof prior to introduction into the PSA unit. Experience has shown that the flammability potential in the system is greatest in the compressor. Therefore, the volume percent of gaseous flame suppressor is at its maximum in the quench tower gaseous phase, i.e. the feed into the compressor, to minimise the flammability potential. The operation conditions of the system are adjusted to provide for this.

The gas phase effluent from the quench tower preferably contains, on a volume basis from about 1 to 3 percent of carbon monoxide, from about 3 to 5 percent of propylene, from about 6 to 8 percent of oxygen, from about 10 to 15 percent of carbon dioxide, and from about 50 to 70 percent of nitrogen and from about 10 to 20 percent of propane, the latter three comprising the gaseous flame suppressor. It must be borne in mind that this example is given relative to the synthesis of acrylonitrile from propylene utilising oxygen-enriched air containing approximately 60 percent by volume of oxygen as the oxygen-containing feed to the ammoxidation reactor which is operating at 60 percent conversion of the propylene. More preferably, the volume percent of propylene, nitrogen and carbon monoxide in the quench tower effluent is from about 35 to 70 percent by volume. In the process illustrated in FIG. 3, the preferred selective separator is a PSA unit operating under pressure provided by a compressor. The compressor increases the pressure of the quench tower gaseous phase to the preferred operating pressure of a PSA unit, typically in the range of from about 122 to 446 kPa (about 3 to 50 psig), preferably from about 239 to 377 kPa (about 20 to 40 psig). The range of preferred operating pressure may vary to an extent depending on the adsorbent utilised.

The adsorbent in the PSA unit may be any material known in the art to adsorb propylene to a substantially greater degree than propane or carbon dioxide. Silica gel is a preferred adsorbent material.

By proper selection of the adsorbent in the PSA unit, the operation thereof can readily be controlled utilising art-recognised manipulations so that the recycle stream formed therein contains a substantial portion of the propylene and lesser percentages of propane and carbon dioxide. The nitrogen, oxygen and the remainder of the carbon oxides and propane are withdrawn from the system, preferably combusted, and vented. It is contemplated herein to recover oxygen from the vent stream and recycle it to the reactor feed to enhance the operation of the system.

Utilising a system, as shown in FIG. 3, for the production of acrylonitrile utilising oxygen-enriched air containing approximately 60 percent by volume of oxygen as a reactor feed and a mixture of nitrogen, carbon dioxide and propane as the gaseous flame suppressor, with nitrogen comprising a major portion thereof, the flow rates in mole percent at critical points in the system were determined and are presented in Table I. The feed was obtained by mixing equal parts of air and pure oxygen. Flow rates were also determined using air as the feed to the ammoxidation reactor and are also reported in Table I. The compositions are expressed in mole percent and based on 100 moles of acrylonitrile produced. The data expressed in Table I represents operation of the system under conditions such that 60 percent and 80 percent, respectively, of the propylene feed to the ammoxidation reactor is converted to products for each feed. In Table I, Point A is the feed into the ammoxidation reactor, Point B is effluent therefrom, Point C is the feed to the compressor, Point D is the recycle stream from the PSA separator, and Point E is the vent

stream from the PSA separator.

TABLE I60 Percent Conversion - Equal parts pure oxygen and air

<u>Component</u>	<u>A</u>	<u>B</u>	<u>C</u>	<u>D</u>	<u>E</u>
Propylene	15.3	5.8	9.2	30.4	0.3
Propane	8.2	7.8	12.4	40.8	0.5
Oxygen	21.1	4.0	6.4	0.4	8.9
CO	---	0.7	1.1	0.1	1.5
CO ₂	4.8	6.5	10.3	24.2	4.4
Acrylonitrile	---	7.2	---	---	---
Acrolein	---	0.1	---	---	---
Acetonitrile	---	0.1	---	---	---
HCN	---	7.2	---	---	---
Water	---	27.3	---	---	---
Ammonia	10.3	1.0	---	---	---
Nitrogen	40.3	38.2	60.6	4.1	84.4

80 Percent Conversion - Equal parts pure oxygen and air

<u>Component</u>	<u>A</u>	<u>B</u>	<u>C</u>	<u>D</u>	<u>E</u>
Propylene	11.7	2.2	3.6	13.6	0.1
Propane	8.4	7.9	12.8	48.3	0.5
Oxygen	21.9	4.0	6.5	0.5	8.5
CO	---	0.8	1.3	---	1.7
CO ₂	5.5	7.5	12.1	33.7	4.9
Acrylonitrile	---	7.2	---	---	---
Acrolein	---	0.1	---	---	---
Acetonitrile	---	0.1	---	---	---
HCN	---	1.6	---	---	---
Water	---	28.0	---	---	---
Ammonia	10.5	1.0	---	---	---

Nitrogen 42.0 39.6 63.7 4.9 84.3

60 Percent Conversion - Air

Component	<u>A</u>	<u>B</u>	<u>C</u>	<u>D</u>	<u>E</u>
Propylene	10.3	4.0	5.4	30.8	0.2
Propane	2.6	2.5	3.4	19.1	0.2
Oxygen	15.6	4.0	5.4	1.6	6.2
CO	---	0.5	0.6	0.2	0.7
CO ₂	3.3	4.5	6.1	25.0	2.2
Acrylonitrile	---	5.0	---	---	---
Acrolein	---	---	---	---	---
Acetonitrile	---	0.1	---	---	---
HCN	---	1.0	---	---	---
Water	---	18.8	---	---	---
Ammonia	7.3	1.0	---	---	---
Nitrogen	60.9	58.6	79.1	23.4	90.5

80 Percent Conversion - Air

Component	<u>A</u>	<u>B</u>	<u>C</u>	<u>D</u>	<u>E</u>
Propylene	7.7	1.5	2.0	10.5	0.2
Propane	1.3	1.3	1.7	9.2	0.2
Oxygen	15.8	4.0	5.4	3.2	5.8
CO	0.1	0.6	0.8	0.5	0.9
CO ₂	3.7	5.0	6.8	27.8	2.5
Acrylonitrile	---	4.8	---	---	---
Acrolein	---	---	---	---	---
Acetonitrile	---	0.1	---	---	---
HCN	---	1.1	---	---	---
Water	---	18.8	---	---	---
Ammonia	7.2	1.0	---	---	---
Nitrogen	64.2	61.8	83.3	48.8	90.4

The data in Table I represents a typical commercial propylene source which comprised about 95 percent propylene with the remainder being propane.

In FIG. 4, there is illustrated a system utilising a pure oxygen feed to the reactor wherein the gaseous flame suppressor comprises propane and carbon dioxide. On a volume-to-volume basis, propane is the most effective component of the subject gaseous flame suppressor mixtures. In the system shown in FIG. 4, the gas phase effluent from the quench tower is introduced into a separator, preferably a PSA unit, to separate the propylene and at least a portion of the propane for recycle to the combined reactor feed. As in the system shown in FIG. 3, the volume percent of propane in the reactor feed is determined so as to produce a concentration in the gaseous feed from the quench tower to the compressor which, in combination with the carbon dioxide present, will minimise flammability potential.

The gas phase effluent from the quench tower preferably contains, on a volume basis, from about 10 to 40 percent of propylene, from about 10 to 25 percent of oxygen, from about 10 to 45 percent of carbon dioxide, from about 2 to 5 percent of carbon monoxide and from about 10 to 50, preferably about 40 percent, of propane. More preferably, the combined volume percent of propylene, propane and carbon monoxide in the quench tower effluent is from about 35 to 70 percent by volume.

The amount of propane in the recycle stream can be the predetermined minimum amount previously given, but typically will be lower to compensate for the amount of propane present in the propylene supply as an impurity. The selective separation capacity of the PSA unit provides not only recycle of a substantial portion of the unreacted propylene to the reactor, but for a relatively constant level of propane in the system.

Utilising a system as shown in FIG. 4 for the production of acrylonitrile utilising a gaseous flame suppressor mixture with propane as major component, the flow rates in mole percent at critical points in the system were determined and are presented in Table II. The compositions are expressed in mole percent and based on 100 moles of acrylonitrile produced. The data expressed in Table II represents operation of the system under conditions such that 60 percent and 80 percent, respectively, of the propylene feed to the ammoxidation reactor is converted to products. In Table II, the various points are the same as in Table I.

TABLE II60 Percent Conversion

<u>Component</u>	<u>A</u>	<u>B</u>	<u>C</u>	<u>D</u>	<u>E</u>
Propylene	27.8	9.3	28.0	39.4	2.3
Propane	8.8	7.4	22.3	28.8	7.4
Oxygen	36.7	5.0	15.0	---	49.1
CO	---	1.0	3.2	---	10.3
CO ₂	8.8	10.5	31.5	31.8	31.0
Acrylonitrile	---	11.6	---	---	---
Acrolein	---	0.1	---	---	---
Acetonitrile	---	0.2	---	---	---
HCN	---	2.3	---	---	---
Water	---	51.5	---	---	---
Ammonia	18.0	1.0	---	---	---

80 Percent Conversion

<u>Component</u>	<u>A</u>	<u>B</u>	<u>C</u>	<u>D</u>	<u>E</u>
Propylene	28.5	9.6	28.7	40.3	2.4
Propane	9.1	7.6	22.8	29.6	7.5
Oxygen	37.6	5.1	15.5	---	50.7
CO	---	1.3	3.8	---	12.4
CO ₂	9.9	11.9	35.7	36.0	35.1
Acrylonitrile	---	11.4	---	---	---
Acrolein	---	0.1	---	---	---
Acetonitrile	---	0.2	---	---	---
HCN	---	2.5	---	---	---
Water	---	52.7	---	---	---
Ammonia	24.7	1.0	---	---	---

The data presented in Table II represents a typical commercial propylene source which comprised about 95 percent propylene with the remainder being propane. The run was repeated utilising high purity propylene which is about 98 percent pure. The results are reported in Table III.

TABLE III

60 Percent Conversion

<u>Component</u>	<u>A</u>	<u>B</u>	<u>C</u>	<u>D</u>	<u>E</u>
Propylene	29.5	9.8	32.6	47.6	2.5
Propane	3.8	3.1	10.4	14.0	3.2
Oxygen	38.5	5.0	16.6	---	50.1
CO	---	1.1	3.7	---	11.1
CO ₂	9.3	11.0	36.7	38.4	33.2
Acrylonitrile	---	12.2	---	---	---
Acrolein	---	0.1	---	---	---
Acetonitrile	---	0.2	---	---	---
HCN	---	2.4	---	---	---
Water	---	54.0	---	---	---
Ammonia	25.0	1.0	---	---	---

80 Percent Conversion

<u>Component</u>	<u>A</u>	<u>B</u>	<u>C</u>	<u>D</u>	<u>E</u>
Propylene	30.2	10.1	33.4	48.8	2.5
Propane	3.8	3.2	10.6	14.3	3.2
Oxygen	39.5	5.1	17.2	---	51.8
CO	---	1.3	4.4	---	13.3
CO ₂	10.5	12.5	41.6	43.6	37.6
Acrylonitrile	---	11.9	---	---	---
Acrolein	---	0.1	---	---	---
Acetonitrile	---	0.2	---	---	---
HCN	---	2.7	---	---	---
Water	---	55.3	---	---	---
Ammonia	25.0	1.0	---	---	---

In the embodiment of the present invention illustrated in FIG. 5, a pure oxygen feed to the ammoxidation reactor is utilised with a gaseous flame suppressor mixture containing carbon dioxide as the major component. In this instance, the percent of carbon dioxide in the feed to the selective separator is from about 25 to 70, preferably from about 35 to 65, percent by volume. The selective separator may be a PSA unit or a conventional liquid separator operating on the well-known Benfield process wherein carbon dioxide is removed from the effluent by dissolution in an absorbent solution, such as potassium carbonate. In either instance, however, although the separator may be run at ambient pressure, it is preferred that the feed to the separator be introduced under pressure utilising, e.g. a compressor, as shown in FIG. 5. When a liquid separator is utilised, the resultant solution is regenerated to release carbon dioxide. Wherein the separator is a PSA unit, the adsorbent is suitably a zeolite molecular sieve such as 4A molecular sieve or a silica gel, preferably the latter.

Since carbon dioxide is produced in the oxidation or ammoxidation reactor as an undesirable by-product, it is preferred to have only a small quantity thereof recycled in the reactor feed. In addition, it is advantageous to minimise the carbon dioxide content in the reactor to prevent an undesirable pressure build-up which would decrease the efficiency of the process. Typically, the feed to the oxidation or ammoxidation reactor comprises propylene, oxygen, ammonia and about 5 percent by volume or less of carbon dioxide.

In the embodiment shown in FIG. 5, carbon dioxide separated in the separator is at least partially recycled upstream of the compressor to assure that the concentration entering the compressor is from about 25 to 70 percent by volume. Since it is not necessary to have a high initial concentration of carbon

dioxide in the reactor, the recycle thereof is within the system to achieve the desired concentration thereof in the gaseous flame suppressor. The recycle may re-enter the system either upstream or downstream of the quench tower or at both locations as shown in FIG. 5. In the event that the concentration of carbon dioxide in the stream entering the compressor becomes too great, a portion of the recycle stream is vented from the system as shown in FIG. 5. The operating pressure of the selective separator is typically from about 10 to 50, preferably from about 20 to 40, psig. The recycle of carbon dioxide as shown in FIG. 5 is carried out even in those instances where the selective separator is operated at close to ambient pressure and there is no compressor in the system since it provides better control over the amount of carbon dioxide in the system.

The gas mixture exiting the selective separator comprises carbon dioxide, carbon monoxide, oxygen and unreacted propylene. A Benfield process selective separator will generally reduce the carbon dioxide content of the effluent gas mixture to about 5 percent by volume. A PSA unit selective separator will generally reduce the carbon dioxide content of the effluent to about 10 percent by volume. Unreacted reactant hydrocarbon is also present in the system to a degree varying with the reactor conversion as disclosed above and is substantially all recycled from the selective separator. Fresh reactant hydrocarbon is added to this mixture to increase the pressure thereof, if necessary, and it is recycled to the ammoxidation reactor where it is combined with incoming oxygen, ammonia and additional reactant hydrocarbon, e.g. propylene, to produce a final carbon dioxide concentration of about 1 percent or less by volume.

Table IV gives an indication of the operating parameters of a system for the synthesis of acrylonitrile as shown in FIG. 5 wherein carbon dioxide is a major component of the gaseous flame suppressor and the selective separator is a conventional liquid separator. As in the previous Tables, the data in Table IV are expressed in mole percent based on 100 moles of acrylonitrile produced. The data in Table IV are also for 60 and 80 percent propylene conversion and are for the following points in the process: A is feed into the ammoxidation reactor; B is effluent therefrom; C is effluent from the quench tower prior to the addition of recycled carbon dioxide thereto; D is the feed to the compressor; E is the recycle stream from the separator to the reactor; and F is the carbon dioxide recycle from the selective separator.

TABLE IV

60 Percent Conversion

<u>Component</u>	<u>A</u>	<u>B</u>	<u>C</u>	<u>D</u>	<u>E</u>	<u>F</u>
Propylene	33.3	11.9	52.4	33.4	65.4	0.8
Propane	1.5	1.3	5.7	3.6	1.9	0.1
Oxygen	42.8	5.0	21.9	14.0	25.9	0.3
CO	1.1	2.0	4.7	3.0	5.6	0.1
CO ₂	0.2	3.7	15.3	45.9	1.2	98.7
Acrylonitrile	---	15.4	---	---	---	---
Acrolein	---	0.1	---	---	---	---
Acetonitrile	---	0.2	---	---	---	---
HCN	---	2.4	---	---	---	---
Water	---	57.0	---	---	---	---
Ammonia	21.1	1.0	---	---	---	---

80 Percent Conversion

<u>Component</u>	<u>A</u>	<u>B</u>	<u>C</u>	<u>D</u>	<u>E</u>	<u>F</u>
Propylene	27.0	4.8	28.4	13.5	28.2	0.2
Propane	1.5	1.4	8.1	3.8	2.1	0.1
Oxygen	47.2	5.0	29.5	14.0	27.8	0.2
CO	1.3	2.2	6.8	3.2	6.4	0.1
CO ₂	0.3	4.9	27.2	65.5	1.8	99.4
Acrylonitrile	---	16.1	---	---	---	---
Acrolein	---	0.1	---	---	---	---
Acetonitrile	---	0.1	---	---	---	---
HCN	---	2.9	---	---	---	---
Water	---	61.5	---	---	---	---
Ammonia	22.7	1.0	---	---	---	---

In Table V, the system is as shown in FIG. 5, but utilising a PSA unit as a separator. In Table IV, points A through D are as in Table IV, Point E is the recycle gaseous stream from the PSA unit, and point F is the CO₂ recycle stream from the PSA unit.

TABLE V

60 Percent Conversion

<u>Component</u>	<u>A</u>	<u>B</u>	<u>C</u>	<u>D</u>	<u>E</u>	<u>F</u>
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Propylene	32.9	11.8	52.2	33.1	63.5	7.4
Propane	1.4	1.3	5.7	3.6	1.8	0.8
Oxygen	43.0	5.0	22.1	14.0	25.4	3.1
CO	1.0	2.0	4.7	3.0	5.4	0.7
CO ₂	0.8	4.1	15.3	46.3	3.9	88.0
Acrylonitrile	---	15.3	---	---	---	---
Acrolein	---	0.1	---	---	---	---
Acetonitrile	---	0.1	---	---	---	---
HCN	---	2.4	---	---	---	---
Water	---	56.9	---	---	---	---
Ammonia	20.9	1.0	---	---	---	---

80 Percent Conversion

Component	A	B	C	D	E	F
Propylene	26.5	4.7	28.3	13.2	39.7	2.2
Propane	1.5	1.3	8.0	3.8	3.0	0.6
Oxygen	47.5	5.0	29.8	14.0	39.7	2.4
CO	1.1	2.2	6.8	3.2	9.0	0.5
CO ₂	1.1	5.5	27.1	65.8	8.6	94.3
Acrylonitrile	---	15.9	---	---	---	---
Acrolein	---	0.1	---	---	---	---
Acetonitrile	---	0.1	---	---	---	---
HCN	---	2.8	---	---	---	---
Water	---	61.4	---	---	---	---
Ammonia	22.3	1.0	---	---	---	---

It will be appreciated that, when carbon dioxide or a substantially unreactive hydrocarbon is the major component of the gaseous flame suppressor in the process of the present invention, it will be necessary initially to add a sufficient amount thereof to the feed to the ammoxidation or oxidation reactor to establish the desired concentration thereof, i.e. to prime the system. This is, however, not necessary utilising oxygen-enriched air as the reactor feed wherein nitrogen is the major component of the gaseous flame suppressor. It will likewise be appreciated that it is within the scope of the present invention to utilise conventional equipment to monitor and automatically regulate the flow of gases within the system so that it can be fully automated to run continuously in an efficient manner.

The process of this invention is advantageous in its simplicity, ease of operation, low capital and operating costs as well as providing a substantially reduced flammability potential. In the process illustrated in FIG. 3, it is possible to utilise a less expensive grade of propylene which contains appreciable quantities of propane as an impurity. Likewise, the use of air or oxygen-enriched air as a starting material wherein nitrogen is the major component of the gaseous flame suppressor, provides further economic savings. The subject process can be run at a relatively low conversion of the feed hydrocarbon to the desired product. To achieve substantially improved selectivity for the subject process. Selectivity is the amount of desired product divided by the total of all products. It will be appreciated that a system that runs at comparatively low conversion and achieves enhanced selectivity to a desired product utilising a less expensive grade of feed materials is highly advantageous.

Claims

1. A process for the production of nitriles and anhydrides comprising:

(a) reacting in a reaction vessel under conditions which produce an effluent containing the nitrile or anhydride at low feed conversion and high selectivity:

either (i) if an anhydride is to be produced, a hydrocarbon and an oxygen-containing gas in the presence of an oxidation catalyst;

or (ii) if a nitrile is to be produced, a hydrocarbon, an oxygen-containing gas, and ammonia in the presence of an ammoxidation catalyst;



Propylene	32.9	11.8	52.2	33.1	63.5	7.4
Propane	1.4	1.3	5.7	3.6	1.8	0.8
Oxygen	43.0	5.0	22.1	14.0	25.4	3.1
CO	1.0	2.0	4.7	3.0	5.4	0.7
CO ₂	0.8	4.1	15.3	46.3	3.9	88.0
Acrylonitrile	---	15.3	---	---	---	---
Acrolein	---	0.1	---	---	---	---
Acetonitrile	---	0.1	---	---	---	---
HCN	---	2.4	---	---	---	---
Water	---	56.9	---	---	---	---
Ammonia	20.9	1.0	---	---	---	---

80 Percent Conversion

Component	<u>A</u>	<u>B</u>	<u>C</u>	<u>D</u>	<u>E</u>	<u>F</u>
Propylene	26.5	4.7	28.3	13.2	39.7	2.2
Propane	1.5	1.3	8.0	3.8	3.0	0.6
Oxygen	47.5	5.0	29.8	14.0	39.7	2.4
CO	1.1	2.2	6.8	3.2	9.0	0.5
CO ₂	1.1	5.5	27.1	65.8	8.6	94.3
Acrylonitrile	---	15.9	---	---	---	---
Acrolein	---	0.1	---	---	---	---
Acetonitrile	---	0.1	---	---	---	---
HCN	---	2.8	---	---	---	---
Water	---	61.4	---	---	---	---
Ammonia	22.3	1.0	---	---	---	---

It will be appreciated that, when carbon dioxide or a substantially unreactive hydrocarbon is the major component of the gaseous flame suppressor in the process of the present invention, it will be necessary initially to add a sufficient amount thereof to the feed to the ammoxidation or oxidation reactor to establish the desired concentration thereof, i.e. to prime the system. This is, however, not necessary utilising oxygen-enriched air as the reactor feed wherein nitrogen is the major component of the gaseous flame suppressor.

It will likewise be appreciated that it is within the scope of the present invention to utilise conventional equipment to monitor and automatically regulate the flow of gases within the system so that it can be fully automated to run continuously in an efficient manner.

The process of this invention is advantageous in its simplicity, ease of operation, low capital and operating costs as well as providing a substantially reduced flammability potential. In the process illustrated in FIG. 3, it is possible to utilise a less expensive grade of propylene which contains appreciable quantities of propane as an impurity. Likewise, the use of air or oxygen-enriched air as a starting material wherein nitrogen is the major component of the gaseous flame suppressor, provides further economic savings. The subject process can be run at a relatively low conversion of the feed hydrocarbon to the desired product. To achieve substantially improved selectivity for the subject process. Selectivity is the amount of desired product divided by the total of all products. It will be appreciated that a system that runs at comparatively low conversion and achieves enhanced selectivity to a desired product utilising a less expensive grade of feed materials is highly advantageous.

Claims

1. A process for the production of nitriles and anhydrides comprising:
 - (a) reacting in a reaction vessel under conditions which produce an effluent containing the nitrile or anhydride at low feed conversion and high selectivity:
 - either (i) if an anhydride is to be produced, a hydrocarbon and an oxygen-containing gas in the presence of an oxidation catalyst;
 - or (ii) if a nitrile is to be produced, a hydrocarbon, an oxygen-containing gas, and ammonia in the presence of an ammoxidation catalyst;



- (b) quenching the effluent with a liquid to form a quenched liquid phase containing said nitrile or anhydride and a gaseous phase containing gaseous products including unreacted hydrocarbon;
(c) recovering said nitrile or anhydride from the liquid phase;
(d) introducing the gaseous phase into a selective separator to thereby remove a substantial portion of the unreacted reactant hydrocarbon; and
(e) recycling said unreacted reactant hydrocarbon to said reactor vessel,
wherein the gaseous phase formed in step (b) contains from 30 to 95 percent by volume of flame suppressor.
- 5
- 10 2. A process according to claim 1, wherein the gaseous mixture formed in step (b) contains from 30 to 75% by volume of flame suppressor.
- 15 3. A process according to claim 1 or claim 2, wherein the oxygen-containing gas is supplied to the reactor in the form of air or a gas enriched in oxygen relative to air, and said gaseous flame suppressor comprises a substantially unreactive hydrocarbon containing 1 to 5 carbon atoms, carbon dioxide and nitrogen.
- 20 4. A process according to claim 3, wherein said substantially unreacted hydrocarbon is a saturated hydrocarbon.
- 25 5. A process according to claim 1 or claim 2, in which pure oxygen is the source of the oxygen-containing gas and the gaseous flame suppressor comprises a substantially unreactive hydrocarbon containing 1 to 5 carbon atoms, and carbon dioxide.
- 30 6. A process according to claim 5, in which the substantially unreactive hydrocarbon is a saturated hydrocarbon.
- 35 7. A process according to any one of the preceding claims, wherein the separation is by pressure swing adsorption.
- 40 8. A process according to claim 7, wherein an adsorbent consisting of a silica gel or a zeolite molecular sieve is employed in the pressure swing adsorption.
- 45 9. A process according to anyone of claims 1 to 8, wherein carbon dioxide is a major component of said gaseous flame suppressor and said separator is a liquid separator wherein carbon dioxide is removed from the gaseous phase by dissolution into an absorbent solution.
- 50 10. A process according to claim 9, wherein the absorbent solution is an aqueous potassium carbonate solution.
- 55 11. A process according to claim 5 or claim 6, wherein at least a portion of the carbon dioxide obtained in said separator is recycled to the effluent formed in step (a), the gas phase formed in step (b) or both of said effluent and said gas phase.
12. A process according to any one of the preceding claims, wherein the nitrile is acrylonitrile, the reactant hydrocarbon is propylene and the gaseous flame suppressor includes propane.
13. A process according to any one of claims 1 to 11, wherein the anhydride is maleic anhydride, the reactant hydrocarbon is n-butane and the gaseous flame suppressor comprises carbon dioxide, isobutane and, where said oxygen-containing gas is air or a gas enriched in oxygen relative to air, nitrogen.
14. A process according to any one of claims 1 and 2 and 5 and 6, wherein the nitrile is acrylonitrile, the reactant hydrocarbon is propylene and the flame suppressor is carbon dioxide and propane, wherein the gas phase formed in step (b) comprises unreacted propylene, oxygen, carbon dioxide, carbon monoxide and from 10 to 50 volume percent of propane, said selective separator is a pressure swing adsorption unit and the gaseous fraction formed therein contains propane and a substantial portion of the unreacted propylene.



Patentansprüche

1. Verfahren zur Herstellung von Nitrilen und Anhydriden, umfassend:

(a) Umsetzen in einem Reaktionsbehälter unter Bedingungen, welche eine das Nitril oder Anhydrid enthaltene Austrittsströmung bei niedriger Einspeisungsumwandlung und hoher Selektivität ergeben:

entweder (i), falls ein Anhydrid erzeugt werden soll, eines Kohlenwasserstoffes und eines sauerstoffhaltigen Gases in Anwesenheit eines Oxidationskatalysators;

oder (ii), falls ein Nitril erzeugt werden soll, eines Kohlenwasserstoffes, eines sauerstoffhaltigen Gases und Ammoniak in Anwesenheit eines Ammonoxidationskatalysators;

(b) Abschrecken der Austrittsströmung mit einer Flüssigkeit zur Bildung einer abgeschreckten, flüssigen Phase, die dieses Nitril oder Anhydrid enthält, und einer gasförmigen Phase, die gasförmige Produkte einschließlich nichtumgesetztem Kohlenwasserstoff enthält;

(c) Gewinnung dieses Nitrils oder Anhydrids aus der flüssigen Phase;

(d) Einführen der gasförmigen Phase in einen selektiven Separator, um hierdurch einen wesentlichen Teil des nichtumgesetzten Reaktionskohlenwasserstoffes zu entfernen; und

(e) Rückführen dieses nichtumgesetzten Reaktionskohlenwasserstoffes zu diesem Reaktionsbehälter, worin die in Stufe (b) gebildete, gasförmige Phase von 30 bis 95 Vol.-% Flammenunterdrückungsmittel enthält.

2. Verfahren nach Anspruch 1, worin die in Stufe (b) gebildete, gasförmige Mischung von 30 bis 75 Vol.-% Flammenunterdrückungsmittel enthält.

3. Verfahren nach Anspruch 1 oder Anspruch 2, worin das sauerstoffhaltige Gas zu dem Reaktor in Form von Luft oder einem relativ zu Luft mit Sauerstoff angereichertem Gas angeliefert wird, und dieses gasförmige Flammenunterdrückungsmittel einen im wesentlichen nicht-reaktionsfähigen Kohlenwasserstoff mit 1 bis 5 Kohlenstoffatomen, Kohlendioxid und Stickstoff umfaßt.

4. Verfahren nach Anspruch 3, worin dieser im wesentlichen nichtumgesetzte Kohlenwasserstoff ein gesättigter Kohlenwasserstoff ist.

5. Verfahren nach Anspruch 1 oder Anspruch 2, in welchem reiner Sauerstoff die Quelle des sauerstoffhaltigen Gases ist, und das gasförmige Flammenunterdrückungsmittel einen im wesentlichen nicht-reaktionsfähigen Kohlenwasserstoff mit 1 bis 5 Kohlenstoffatomen und Kohlendioxid umfaßt.

6. Verfahren nach Anspruch 5, in welchem der im wesentlichen nicht-reaktionsfähige Kohlenwasserstoff ein gesättigter Kohlenwasserstoff ist.

7. Verfahren nach einem der vorhergehenden Ansprüche, worin die Trennung durch Druckwechseladsorption erfolgt.

8. Verfahren nach Anspruch 7, worin ein aus einem Kieselgel oder einem Zeolith-Molekularsieb bestehendes Adsorptionsmittel bei der Druckwechseladsorption eingesetzt wird.

9. Verfahren nach einem der Ansprüche 1 bis 8, worin Kohlendioxid eine Hauptkomponente dieses Flammenunterdrückungsmittels ist, und dieser separator ein Flüssigkeitsseparator ist, worin Kohlendioxid aus der gasförmigen Phase durch Auflösen in einer Absorptionsmittellösung entfernt wird.

10. Verfahren nach Anspruch 9, worin die Absorptionsmittellösung eine wässrige Kaliumkarbonatlösung ist.

11. Verfahren nach Anspruch 5 oder Anspruch 6, worin wenigstens ein Teil des in diesem Separator erhaltenen Kohlendioxids zu der in Stufe (a) gebildeten Austrittsströmung, der in Stufe (b) gebildeten Gasphase oder zu beiden von dieser Austrittsströmung und dieser Gasphase rückgeführt wird.

12. Verfahren nach einem der vorhergehenden Ansprüche, worin das Nitril Acrylnitril ist, der Reaktionskohlenwasserstoff Propylen ist, und das gasförmige Flammenunterdrückungsmittel Propan einschließt.



13. Verfahren nach einem der Ansprüche 1 bis 11, worin das Anhydrid Maleinanhydrid ist, der Reaktionskohlenwasserstoff n-Butan ist, und das gasförmige Flammenunterdrückungsmittel Kohlendioxid, Isobutan und, falls das sauerstoffhaltige Gas Luft oder ein relativ zu Luft mit Sauerstoff angereichertes Gas ist, Stickstoff umfaßt.

14. Verfahren nach einem der Ansprüche 1 und 2 und 5 und 6, worin das Nitril Acrylnitril ist, der Reaktionskohlenwasserstoff Propylen ist, und das Flammenunterdrückungsmittel Kohlendioxid und Propan ist, wobei die in Stufe (b) gebildete Phase nichtumgesetztes Propylen, Sauerstoff, Kohlendioxid, Kohlenmonoxid und von 10 bis 50 Vol.-% Propan umfaßt, dieser selektive Separator eine Druckwechseladsorptionseinheit ist und die hierin gebildete, gasförmige Fraktion Propan und einen wesentlichen Anteil des nichtumgesetzten Propylens enthält.

Revendications

1. Procédé pour la production de nitriles et d'anhydrides, ce procédé comprenant :
 - (a) la réaction, dans un réacteur dans des conditions qui produisent un effluent contenant le nitrile ou l'anhydride à un faible taux de conversion de l'alimentation et avec une sélectivité élevée :
 - (i) si un anhydride doit être produit, d'un hydrocarbure et d'un gaz contenant de l'oxygène, en présence d'un catalyseur d'oxydation ;
 - ou (ii) si un nitrile doit être produit, d'un hydrocarbure, d'un gaz contenant de l'oxygène, et de l'ammoniac en présence d'un catalyseur d'ammoxydation ;
 - (b) le refroidissement de l'effluent à l'aide d'un liquide pour former une phase liquide refroidie contenant ledit nitrile ou ledit anhydride et une phase gazeuse contenant des produits gazeux comprenant l'hydrocarbure n'ayant pas réagi ;
 - (c) la récupération dudit nitrile ou anhydride à partir de la phase liquide ;
 - (d) l'introduction de la phase gazeuse dans un séparateur sélectif pour enlever ainsi une forte proportion de l'hydrocarbure introduit pour réagir et qui n'a pas réagi ; et
 - (e) le recyclage de cet hydrocarbure, introduit pour réagir et qui n'a pas réagi, vers ledit réacteur, la phase gazeuse formée dans l'étape (b) contenant de 30 à 95 % en volume d'un suppresseur de flamme.
2. Procédé selon la revendication 1, dans lequel le mélange gazeux formé dans l'étape (b) contient de 30 à 75 % en volume du suppresseur de flamme.
3. Procédé selon la revendication 1 ou 2, dans lequel le gaz contenant de l'oxygène est fourni au réacteur sous la forme d'air ou d'un gaz enrichi en oxygène par rapport à l'air, et ledit suppresseur gazeux de flamme comprend un hydrocarbure sensiblement non réactif contenant 1 à 5 atomes de carbone, du dioxyde de carbone et de l'azote.
4. Procédé selon la revendication 3, dans lequel ledit hydrocarbure n'ayant sensiblement pas réagi est un hydrocarbure saturé.
5. Procédé selon la revendication 1 ou à la revendication 2, dans lequel l'oxygène pur constitue la source du gaz contenant de l'oxygène, et le suppresseur gazeux de flamme comporte un hydrocarbure sensiblement non réactif contenant 1 à 5 atomes de carbone, et du dioxyde de carbone.
6. Procédé selon la revendication 5, dans lequel l'hydrocarbure sensiblement non réactif est un hydrocarbure saturé.
7. Procédé selon l'une quelconque des revendications précédentes, dans lequel la séparation est effectuée par adsorption avec variation cyclique de pression.
8. Procédé selon la revendication 7, dans lequel on utilise, dans l'adsorption avec variation cyclique de pression, un adsorbant consistant en un gel de silice ou en un tamis moléculaire zéolitique.
9. Procédé selon l'une quelconque des revendications 1 à 8, dans lequel le dioxyde de carbone forme un constituant majeur dudit suppresseur gazeux de flamme, et ledit séparateur est un séparateur à liquide dans lequel le dioxyde de carbone est enlevé de la phase gazeuse par dissolution dans une solution



absorbante.

10. Procédé selon la revendication 9, dans lequel la solution absorbante est une solution aqueuse de carbonate de potassium.

11. Procédé selon la revendication 5 ou la revendication 6, dans lequel au moins une partie du dioxyde de carbone obtenu dans ledit séparateur est recyclée vers l'effluent formé à l'étape (a), la phase gazeuse formée à l'étape (b) ou à la fois vers ledit effluent et ladite phase gazeuse.

12. Procédé selon l'une quelconque des revendications précédentes, dans lequel le nitrile est l'acrylonitrile, l'hydrocarbure à faire réagir est le propylène, et le suppresseur gazeux de flamme comporte du propane.

13. Procédé selon l'une quelconque des revendications 1 à 11, dans lequel l'anhydride est l'anhydride maléique, l'hydrocarbure à faire réagir est le n-butane et le suppresseur gazeux de flamme comprend du dioxyde de carbone, de l'isobutane et, lorsque ledit gaz contenant de l'oxygène est de l'air ou est un gaz enrichi en oxygène par rapport à l'air, de l'azote.

14. Procédé selon l'une quelconque des revendications 1 et 2 et 5 et 6, dans lequel le nitrile est l'acrylonitrile, l'hydrocarbure à faire réagir est le propylène, et le suppresseur de flamme est du dioxyde de carbone et du propane ; la phase gazeuse formée à l'étape (b) comprend du propylène n'ayant pas réagi, de l'oxygène, du dioxyde de carbone, du monoxyde de carbone et de 10 à 50 % en volume de propane, ledit séparateur sélectif est une unité d'adsorption avec variation (cyclique) de la pression et la fraction gazeuse qui y est formée contient du propane et une forte proportion du propylène n'ayant pas réagi.