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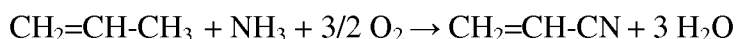
(54) **Title:** ACRYLONITRILE REACTOR STARTUP PROCEDURE

(57) **Abstract:** Formation of explosive mixtures during start up of an acrylonitrile reactor is prevented by including ammonia in the gases charged into the reactor during catalyst preheating. In addition to generating heat, oxidation of this ammonia reduces the oxygen content of the gas inside the acrylonitrile reactor, as well as in the reactor effluent gas, thereby reducing the risk that explosive mixtures will form in this effluent gas.

## ACRYLONITRILE REACTOR STARTUP PROCEDURE

### Background

In the commercial manufacture of acrylonitrile, propylene, ammonia and oxygen are reacted together according to the following reaction scheme:



This process, which is commonly referred to as ammoxidation, is carried out in the gas phase at elevated temperature in the presence of a suitable fluid bed ammoxidation catalyst.

Fig. 1 illustrates a typical ammoxidation reactor used to carry out this process. As shown there, reactor 10 comprises reactor shell 12, air grid 14, feed sparger 16, cooling coils 18 and cyclones 20. During normal operation, process air is charged into reactor 10 through air inlet 22, while a mixture of propylene and ammonia is charged into reactor 10 through feed sparger 16. The flow rates of both are high enough to fluidize a bed 24 of ammoxidation catalyst in the reactor interior, where the catalytic ammoxidation of the propylene and ammonia to acrylonitrile occurs.

Product gases produced by the reaction exit reactor 10 through reactor effluent outlet 26. Before doing so, they pass through cyclones 20, which remove any ammoxidation catalyst these gases may have entrained for return to catalyst bed 24. Ammoxidation is highly exothermic, and so cooling coils 18 are used to withdraw excess heat and thereby keep the reaction temperature at an appropriate level.

As further discussed below, one of the early steps in the start-up of an acrylonitrile reactor is to preheat the ammoxidation catalyst to elevated temperature. For this purpose, start-up heater 28 is provided to heat the process air being fed to air inlet 22 during this catalyst preheating step.

Propylene and ammonia, as well as the combustible components of the reactor effluent gas, *e.g.*, acrylonitrile, unreacted propylene, unreacted ammonia, hydrogen cyanide, acrolein, acrylic acid and acetonitrile, can form explosive mixtures with oxygen. Accordingly, care must be taken during normal operation, as well as during start up, to avoid situations where explosions can occur. During normal operation, inside the reactor at normal operating temperatures, this is not a concern because the ammoxidation reaction prevents explosions from occurring. Therefore, reactor 10 is designed and operated so that the only place process air is allowed to

contact propylene and ammonia during normal operation is within the fluidized bed of ammoxidation catalyst 24, and then only when the temperature of the catalyst is high enough to catalyze the ammoxidation reaction.

During start up and shut down, however, the temperature of the ammoxidation catalyst is usually not high enough to prevent explosion. Therefore, different approaches are normally taken to prevent explosion, all of which are based on the idea of avoiding formation of explosive mixtures in the first place.

In this regard, to be explosive, a mixture of a combustible ingredient and oxygen needs to contain a certain minimum concentration of the combustible ingredient, which is referred to as the “lower flammability limit” concentration of that ingredient. In addition, the mixture must also contain a certain minimum concentration of oxygen to support the combustion of the combustible ingredient, which is referred to as the “limiting oxygen concentration” of the mixture. Accordingly, earlier approaches for avoiding explosive mixtures during start-up rely either on a “fuel limited approach” in which the concentration of combustible ingredients is kept below their lower flammability limit concentrations, or on an “oxygen limited approach” in which the concentration of oxygen is kept below its limiting oxygen concentration, in all relevant gas mixtures.

For example, in a typical oxygen limited approach for starting up an acrylonitrile reactor, heated process air is used to preheat the catalyst to a suitable elevated temperature. Once this occurs, the flow of heated process air is replaced with the flow of heated inert gas, typically steam or nitrogen, until the concentration of oxygen in the reactor effluent gas drops to a safe level, *i.e.*, a level below the limiting oxygen concentration of the effluent gas during normal operation. Only after this occurs is the flow of propylene and ammonia to the reactor started. Explosive mixtures do not form in the reactor effluent gas, because the concentration of oxygen in the reactor effluent gas drops below its limiting oxygen concentration before combustible ingredients such as acrylonitrile, HCN, unreacted propylene and unreacted ammonia appear in this effluent gas.

Steam can have an adverse effect on the ammoxidation catalyst and reactor internals, and so steam is not preferred for this purpose. While these problems are avoided if nitrogen is used as the inert gas, large amounts of nitrogen are required which can be cost prohibitive in many

situations. Accordingly, using an oxygen limited approach for avoiding explosive gases during start-up of an acrylonitrile reactor is not used very often due to these undesirable features.

In a typical fuel limited approach for starting up an acrylonitrile reactor, heated process air is also used to preheat the catalyst to a suitable elevated temperature. Once this temperature is reached, the flow of propylene and ammonia to the reactor is started, but this is done only very slowly. Because these reactants are rapidly consumed by the ammoxidation reaction, and further because their flowrates are low, the concentrations of combustible ingredients in the reactor effluent gas always remain below their lower flammability limit concentrations. So, the idea of this approach is that, so long as the flowrates of propylene and ammonia to the reactor during start-up are low, the amount of combustible ingredients appearing in the reactor effluent gas will always be less than their lower flammability limit concentrations, even though the concentration of oxygen in the reactor as well as in the reactor effluent gas is relatively high.

A problem with this fuel limited approach, however, is that once the system achieves normal operating conditions, explosive mixtures are prevented in the effluent gas because the oxygen concentration in this gas is too low, not because the concentrations of combustible ingredients are too low. This means that when this approach is used, the system transitions between a fuel limited approach for avoiding explosive mixtures to an oxygen limited approach as the system progresses from start-up to normal operation. The problem is that, during this transition, the concentrations of combustible ingredients in the effluent gas, on the one hand, and the oxygen in this effluent gas, on the other hand, can get quite close to one another in terms of producing an explosive mixture.

In this regard, it should be remembered that the lower flammability limit concentration of a combustible ingredient in a gas mixture and the corresponding limiting oxygen concentration in that gas mixture vary inversely with respect to one another. That is to say, if the oxygen concentration of the gas mixture increases, then the lower flammability limit concentration of the combustible ingredient in that gas mixture decreases, and conversely. In addition, the flammability envelope of a combustible ingredient (*i.e.*, the difference its upper and lower flammability limits) in a gas mixture as well as the difference between the maximum and minimum limiting oxygen concentrations of the mixture increase with increasing temperature.

Accordingly, when the system transitions between a fuel limited approach for avoiding explosive mixtures during early stages of start-up to an oxygen limited approach during late

stages of start-up, there may come a time when the concentrations of combustible ingredients and oxygen in the effluent gas get quite close to one another in terms of producing an explosive mixture. As a result, not only is precise control of the reaction temperature as well as the propylene and ammonia feed rates required if this approach is used, but in addition there is still a fairly high risk that the effluent gas can become explosive even if this precise control is provided.

Making this problem even worse is that the fact that the products and by products of the ammoxidation reaction, (*e.g.*, acrylonitrile, HCN, acetonitrile, acrylic acid and acrolein) are also combustible. So even though the effluent gas may not be explosive with respect to propylene or ammonia, it still may be explosive with respect to these products and by-products.

Still another problem with this fuel limited approach is that some of the products and by-products of the ammoxidation reaction, *e.g.*, acrolein, while not explosive if present in low enough concentration, are nonetheless still unstable at the temperatures and oxygen concentrations encountered in the reactor effluent gas. This instability can lead to a combustion reaction occurring in the effluent gas (known as “effluent afterburning”), which results in undesirable high effluent temperature.

### **Summary of the Invention**

In accordance with this invention, new procedures are provided for avoiding formation of explosive mixtures during start-up, which new procedures are easier and less expensive to perform than similar procedures carried out in the past.

A start-up process for an acrylonitrile reactor includes charging an ammoxidation catalyst into at least one ammoxidation reactor; heating the ammoxidation catalyst to at least a minimum ammonia oxidation temperature; and introducing ammonia and optionally propylene into the reactor, wherein a propylene to ammonia molar ratio of about 0 to about 0.02 is maintained in a reactor effluent until the oxygen concentration in the reactor effluent is below a limiting oxygen concentration.

In another aspect, a start-up process for an acrylonitrile reactor includes charging an ammoxidation catalyst into at least one ammoxidation reactor; heating the ammoxidation catalyst to at least a minimum ammonia oxidation temperature; and introducing ammonia and optionally propylene into the reactor in amounts effective for increasing catalyst temperature to an interim

reaction temperature of about 415 °C to about 425°C, wherein propylene is introduced into the reactor in an amount effective for preventing an unstable exothermic reaction.

In one aspect, a process for producing acrylonitrile includes charging an ammoxidation catalyst into at least one ammoxidation reactor; heating the ammoxidation catalyst to at least a minimum ammonia oxidation temperature; introducing ammonia into the reactor in an amount effective for providing an oxygen concentration in the reactor below a limiting oxygen concentration; and introducing propylene into the reactor in an amount effective for producing acrylonitrile. The process may include maintaining a propylene to ammonia ratio of about 0 to about 0.02 until the oxygen concentration in the reactor is below the limiting oxygen concentration.

In another aspect, a process for starting up an acrylonitrile reactor containing a new charge of a bismuth molybdate ammoxidation catalyst, a method for reducing sublimation of molybdenum, the method includes introducing propylene and ammonia to the reactor in an amount effective for increasing a temperature of the catalyst from an interim reaction temperature of about 415° C to about 425° C to a steady state reaction temperature of about 435° C to about 445° C over a period of time of about 1 to about 400 hours

In another aspect, this invention provides a new process for heating an air-fluidized ammoxidation catalyst during start up of an acrylonitrile reactor in a manner which avoids forming an explosive gas mixture, the process comprising

- (a) preheating the air-fluidized ammoxidation catalyst to an ammonia-active temperature high enough so that the catalyst will catalyze the oxidation of ammonia to nitrogen and water,
- (b) thereafter including ammonia in the gases being charged into the reactor to generate additional heat for catalyst preheating through the catalytic oxidation of ammonia, wherein the flow of ammonia charged into the reactor is sufficient to reduce the concentration of oxygen in the reactor effluent gas to below the limiting oxygen concentration of this effluent gas, *i.e.*, to a concentration which is so low that effluent gas is no longer explosive due to insufficient oxygen, and
- (c) delaying the feed of propylene to the ammoxidation catalyst until the concentration of oxygen in the reactor effluent gas has been reduced to below its limiting oxygen concentration.

Preferably, ammonia addition is step (b) begins when the temperature of the ammoxidation catalyst reaches about 380° C, about 365° C, or even about 350° C. In addition, it is also preferable that, once this ammonia addition begins, the amount of ammonia charged into the reactor is sufficient to lower the concentration of oxygen in the reactor effluent gas to below 10 vol.% or even below 8 vol. % before propylene feed to the reactor begins.

In addition, preheating of the ammoxidation catalyst in step (a) is preferably carried out using a direct-fired in-line heater rather than the indirect fired heaters normally used for this purpose, as this further reduces the concentration of oxygen inside the reactor as well as in the reactor effluent gas significantly.

In addition to the above ammonia-assisted catalyst heating procedure, this invention also provide a new sparger purging process for avoiding plugging or contamination of the feed sparger during a reactor startup which uses this ammonia-assisted catalyst heating procedure, this sparger purging process comprising using air to purge the feed sparger during the initial phases of start-up and then changing the gas used to purge the sparger from air to nitrogen shortly before ammonia feed to the reactor begins.

## **DETAILED DESCRIPTION OF THE INVENTION**

Start up of a commercial fluidized bed acrylonitrile reactor begins with the ammoxidation catalyst being in a quiet (unfluidized) condition, resting on top of air grid 14 of the reactor. In one aspect, a single reactor may be used, in another aspect more than one reactor may be used, in another aspect, two reactors may be used. Reactor effluents may be combined at later points in the process.

The first step of a typical reactor start-up procedure involves a nitrogen purge of the feed sparger, *i.e.* charging nitrogen gas through the feed sparger at a flowrate sufficient to prevent fluidized ammoxidation catalyst from entering or plugging the sparger. At the same time, or shortly thereafter, heated process air is fed to air inlet 22 at a flowrate sufficient to cause the ammoxidation catalyst to fluidize. This heating step is continued until the temperature of the ammoxidation catalyst reaches or slightly exceeds its minimum ammoxidation temperature, which typically takes 8 to 16 hours, primarily depending on the size of the reactor. Once this temperature is reached, the system is changed to normal operating conditions by terminating the heating of the incoming process air, replacing the nitrogen being charged through the feed

sparger with a mixture of propylene and ammonia, and adjusting the flowrate of the incoming process air to its normal operating value. To prevent explosive mixtures from forming, additional steps as described in the background section of this disclosure are taken.

In accordance with this invention, a fuel limited approach is also used to avoid formation of explosive gas mixtures in the reactor effluent gases during start-up. However, the fuel limited approach of this invention differs from the fuel limited approach described in the background section of this document in that the flow of ammonia to the feed sparger begins as soon as, or shortly after, the temperature of the ammoxidation catalyst is high enough to catalyze the oxidation of ammonia to nitrogen and water (its "ammonia-active temperature") rather than simultaneously with the propylene feed as occurs in conventional practice. As a result, before propylene is fed to the reactor, the concentration of oxygen in the reactor effluent gas can be reduced to a level which is so low that this gas is no longer explosive due to an insufficient oxygen concentration.

The lower flammability limit concentration of ammonia is significantly higher than the lower flammability limit concentration of propylene at a given concentration of oxygen. In other words, for a given concentration of oxygen, a gas mixture can tolerate a greater amount of ammonia than propylene before becoming explosive. In accordance with this invention, therefore, feeding of ammonia into the reactor is started at earlier stages of start-up than would otherwise be the case and, in addition, before feeding of propylene begins. Although the oxygen concentration in the effluent gas is higher at these earlier stages of start-up than at later states, this is not of significant concern because the effluent gas can tolerate a greater concentration of ammonia than propylene before becoming explosive.

Accordingly, this early introduction of ammonia is used to cause the oxygen concentration of the effluent gas to drop to a safe level (*i.e.*, below its limiting oxygen concentration during normal operations) before the feed of propylene to the reactor begins. The limiting oxygen concentration of a mixture of propylene in air at the elevated temperatures experienced by the effluent gas during normal operations (*e.g.*, ~440° C) is not known exactly, but is estimated to be between ~8 to ~10 vol.%. Therefore, in accordance with this invention, early introduction of ammonia is continued until the oxygen concentration of the effluent gas drops to about 10 volume % or less, in another aspect, about 9 volume % or less, in another



aspect, about 8 volume % or less, in another aspect, about 7 volume % or less, and in another aspect, about 6 volume % or less, before the feed of propylene to the reactor begins.

The practical effect of this approach is that the risk that explosive mixtures will form in the reactor effluent gas as the system transitions from a fuel-limited regimen during start-up to an oxygen-limited regimen during normal operations is eliminated essentially completely. This is because a target oxygen concentration of 8 vol.% or less is below the limiting oxygen concentration of a propylene/oxygen gas mixture at the elevated temperatures the effluent gas will experience, while the preferred target oxygen concentrations of about 6-7 vol.% is farther below this limiting oxygen concentration. Accordingly, by delaying introduction of propylene until the oxygen content of the system is this low, a propylene explosion cannot occur regardless of the amount of propylene the effluent gas may ultimately contain due to insufficient oxygen being present. In another aspect, small amounts of propylene may be introduced without any delay. In this aspect, a propylene to ammonia ratio of about 0 to about 0.02 is maintained until the oxygen concentration in the reactor is below the limiting oxygen concentration. In another aspect, a propylene to ammonia ratio of about 0.001 to about 0.02, in another aspect, about 0.005 to about 0.02, in another aspect, about 0.01 to about 0.02, and in another aspect, about 0.015 to about 0.02 is maintained.

In a preferred embodiment of this invention, a direct-fired in-line heater is used for heating the process air being fed to the reactor for preheating the catalyst. In this context, a "direct-fired in-line heater" means a combustion furnace which is structured so that the combustion gases generated by the furnace are included in the heated process air produced by the furnace which is being fed to reactor 10. Direct-fired in-line heaters are different from the indirect fired heaters normally used for heating process air during start-up in that indirect fired heaters discharge their combustion products to waste rather than combining them with the heated process air they produce.

When an indirect fired heater heats the process air used for catalyst preheating, this process air and hence the air inside the reactor as well as the reactor effluent gas have the same oxygen concentration as normal air, *i.e.*, ~21 vol.%. In contrast, the heated process air produced by a direct-fired in-line heater contains only ~18 vol.% oxygen. Accordingly, when a direct-fired in-line heater heats the process air used for catalyst preheating, the air inside the reactor and in the reactor effluent gas at the beginning of start-up has an oxygen concentration of only ~18

vol.%. This, in turn, means when the system transitions between a fuel limited approach during early stages of start-up to an oxygen limited approach during later stages of start-up, this transition begins with ~3 vol.% less oxygen if a direct-fired in-line heater is used instead of an indirect fired heater. Inasmuch as the limiting oxygen concentration of the reactor effluent gas during normal operation is above 8 vol. %, this ~3 vol.% reduction from ~21 vol.% to ~18 vol.% in the beginning oxygen concentration represents a 23% reduction ( $3/(21-8)$ ) in the amount by which the oxygen concentration needs to be reduced during this transition to avoid explosive mixtures from forming in the effluent gas.

The practical effect of this reduction is not only that the limiting oxygen concentration of the effluent gas is reached sooner than would otherwise be the case, but also that the concentrations of combustible ingredients in the effluent gas do not come as close to their lower flammability limit concentrations as would otherwise be the case. As a result, the reaction temperature as well as the propylene and ammonia feed rates during this critical transition period do not need to be as precisely controlled as previously required to insure that explosive risks in the effluent gas are avoided.

In accordance with another feature of this invention, air is used for purging the feed sparger 16 during the initial stages of start-up instead of the nitrogen gas which is conventional used for this purpose. Then, shortly before ammonia feed to the reactor begins, the gas used to purge the sparger is changed from air to nitrogen. In this context, "shortly before" will be understood to mean within 30 minutes before ammonia feed is started. Embodiments in which the change of the sparger feed from air to nitrogen occurs with 20 minutes before, within 10 minutes before, or even within 5 minutes before, the gas used to purge the sparger is changed from air to nitrogen are also contemplated. The advantage of this approach over conventional practice in which nitrogen is used for the entire sparger purging process is that significant amounts of nitrogen are saved.

An example of a detailed ammoxidation reactor start-up procedure using the principles of this invention is described below:

#### Prestart-up

Before start-up begins, all downstream and ancillary equipment (*e.g.*, quench, absorber, recovery column, vaporizers, steam system, utilities, etc.) as well as all necessary reactor

instrumentation (*e.g.*, reactor temperature sensors, feed flow sensors, and oxygen analyzers for the reactor effluent) are made ready for service. In addition, the fluid-bed ammoxidation catalyst is charged into the reactor and is in a quiet (unfluidized) state, resting on air grid 14. The process air feed compressor is then started and set to vent to the atmosphere.

#### Sparger Purge

A flow of nitrogen gas, or air if desired, is introduced into sparger 16 to keep fluidized catalyst from plugging or otherwise contaminating the sparger.

#### Establishing Air Flow to Reactor

Ammoxidation catalyst 24 in reactor 10 is then fluidized by slowly opening the reactor air flow controller (not shown) to begin and then increase the flow of process air through start-up heater 28, reactor 10, and the associated downstream equipment (not shown). Normally, the flowrate of process air will be increased until it reaches normal operating conditions. In this context, “normal operating conditions” means the conditions experienced in reactor 10 after start-up is completed and the ammoxidation reaction proceeds in a normal, steady state condition.

#### Activating the Start-up Heater

After process air flow has been established to reactor 10, start-up heater 28 is started and operated so that the temperature of the process air exiting the heater is above the minimum ammonia oxidation temperature of the ammoxidation catalyst. In practice the temperature exiting the air start-up heater 28 will be operated to achieve the highest process air temperature possible, typically about 480° – 500° C, as this enables the catalyst to be preheated as quickly as possible, which typically takes about 8 to 12 hours depending on reactor size.

While start-up heater 28 can be an indirect-fired heater, an in-line, direct-fired type heater is desirably used for this purpose for the reasons indicated above, *i.e.*, because such a heater reduces the concentration of oxygen in the reactor effluent gas at the beginning of start-up to ~18 vol.% as opposed to the normal ~21 vol.% that would be achieved if an indirect fired heater were used.

### Preheating the Catalyst

The flow of heated process air into reactor 10 is continued at least until the temperature of the ammoxidation catalyst reaches its minimum ammonia oxidation temperature, *i.e.*, the minimum temperature at which the ammoxidation catalyst is capable of catalyzing the oxidation of ammonia to nitrogen and water, which is typically about 180° C to 200° C. Typically, however, the heated process air will be used to preheat the ammoxidation catalyst to a much higher temperature, for example, to at least 350° C, at least 375° C or even at least 390° C, as this reduces the amount of ammonia that is needed in the subsequent ammonia combustion steps discussed below, which is more economic.

### Preparation for Initial Ammonia Introduction

Shortly before ammonia is introduced into the reactor, the flowrate of process air can be reduced somewhat, if desired, as this reduces the amount of ammonia needed in this and the following ammonia introduction steps. Flowrate reductions which occur within 30 minutes before, within 20 minutes before, or even within 10 minutes before ammonia is first introduced into the reactor are contemplated, as are reductions which achieve a process air flowrate of 30-95%, 40-85% or even 50-75% of the process air flowrate during normal operating conditions.

In addition to this optional reduction in process air flowrate, if air is used as purging gas for preventing contamination of sparger 16 as described above in connection with one embodiment of this invention, this airflow through sparger 16 needs to be discontinued and replaced with nitrogen as the purging gas before ammonia introduction begins. If air flowrate is reduced, it is maintained at its reduced flowrate during the initial and continued ammonia feed introduction, while the reactor effluent gas oxygen concentration is being reduced. When the propylene feed is first introduced and then increased in stepwise fashion, air flowrate and ammonia flowrate are also increased in stepwise fashion until the propylene, air, and ammonia feedrates reach their normal, final values.

### Initial Ammonia Introduction

Once all of the air is purged from sparger 16, the flow of ammonia into reactor 10 through feed sparger 16 is initiated and increased to a suitable level, preferably stepwise to facilitate reactor temperature control. As discussed above, this causes ammoxidation catalyst 24

in reactor 10 to catalytically oxidize this ammonia feed into nitrogen gas and water. One result of this oxidation reaction is that the amount of oxygen in reactor 10 and hence the reactor effluent gas passing out of the reactor decreases significantly. Another result of this oxidation reaction is that a significant amount of heat is generated, which contributes to catalyst preheating thereby reducing the amount of propylene required for this purpose. Cooling coils 18 can be put into service to control the temperature of ammoxidation catalyst inside reactor 10, as necessary. While the temperature inside the reactor can be allowed to rise somewhat, it is desirably kept at or near the reactor temperature encountered during normal operations, which is typically on the order of 350° C to 480° C.

In a particular example of this initial ammonia introduction, the flowrate of ammonia feed can be initially set at a low level, for example at a value to give an air-to-ammonia molar feed ratio of 13 to 15. At this initial low ammonia feed rate, the ammonia concentration in the reactor effluent gas will be about 6 – 7%, which is well below its lower flammability limit concentration in air. Once ammonia oxidation begins, as will be evident from the oxygen concentration in the reactor effluent gas, the ammonia feed rate can be further increased.

If desired, heating of incoming process air by means of start-up heater 28 can be discontinued when the feed of ammonia to the reactor begins or shortly thereafter. However, as further discussed below, it is more desirable to keep the start-up heater operating until propylene introduction into the reactor reaches its final desired flowrate, as this can reduce the cost of ammonia needed for catalyst preheating significantly.

#### Continued ammonia feed introduction

The flowrate of ammonia into reactor 10 through sparger 16 can be increased all at once or continuously. Desirably, the ammonia flowrate is increased in steps, for better reactor temperature control, as mentioned above. The flowrate of the ammonia feed is increased relative to the flowrate of incoming process air until the oxygen concentration in the reactor effluent gas drops below the target values of 8 vol.%, which is below the limiting oxygen concentration for propylene in this effluent gas. Preferably, the flowrate of the ammonia feed is increased until the oxygen concentration in the reactor effluent gas drops to ~6 to ~7 vol.%. In practice, an oxygen concentration in the reactor effluent gas of ~7 vol.% corresponds to an air-to-ammonia volume feed ratio of about 5.

### Propylene feed introduction

When the concentration of oxygen in the reactor effluent gas decreases to the desired value of less than 8 vol.%, preferably ~6 to ~7 vol.%, the flow of propylene into reactor 10 through sparger 16 is started. Thereafter, the propylene flowrate is increased, desirably in stepwise fashion to enable precise reactor temperature control, until the final desired propylene flowrate is achieved. At this time, start-up heater 28 can be shut down, if not done previously.

In one aspect, a start-up process for an acrylonitrile reactor includes charging an ammoxidation catalyst into at least one ammoxidation reactor. The process includes heating the ammoxidation catalyst to at least a minimum ammonia oxidation temperature. In this aspect, ammonia and optionally propylene is introduced into the reactor when the ammoxidation catalyst has reached a minimum ammonia oxidation temperature of about 350 °C or more, in another aspect, about 350 °C to about 480 °C, in another aspect, about 375 °C to about 450 °C, and in another aspect, about 400 °C to about 425 °C. In another aspect, a propylene to ammonia molar ratio of about 0 to about 0.02 is maintained in a reactor effluent until the oxygen concentration in the reactor effluent is below a limiting oxygen concentration, in another aspect, a ratio of about 0 to about 0.01 is maintained, and in another aspect, a ratio of about 0.01 to about 0.02 is maintained.

In another aspect, the process includes maintaining a propylene to ammonia molar ratio of about 0 in the reactor effluent until the oxygen concentration in the reactor effluent is below the limiting oxygen concentration. In another aspect, the limiting oxygen concentration in the reactor effluent may be about 10 volume % or less, in another aspect, about 9 volume % or less, in another aspect, about 8 volume % or less, in another aspect, about 7 volume % or less. In another aspect, a propylene:ammonia ratio in the reactor effluent is about 0 when the oxygen concentration in the reactor effluent is about 12 volume % or more. In a related aspect, a propylene:ammonia ratio in the reactor effluent is about 0.02 or more when the oxygen concentration in the reactor effluent is about 7 volume % or less. In some aspect, the oxygen concentration in reactor effluent may be kept at a concentration of least about 0.5 volume % or more, in another aspect, about 0.5 volume % to about 7 volume %, in another aspect, about 0.5 volume % to about 1.5 volume %, and in another aspect, about 0.5 volume % to about 2 volume

%. Oxygen concentration in the reactor effluent may be measured by any know method, such as for example by a continuous in-line oxygen meter.

#### Acrylonitrile Plants with Multiple Reactors

In a typical commercial acrylonitrile plant, the hot reactor effluent gases passing out of reactor 10 is first passed into a quench column where they are sprayed with acidified water. This not only reduces the temperature of the effluent gases to a safe and manageable level but also neutralizes any unreacted ammonia that still might be present. The cooled reactor effluent gases, now purged of their unreacted ammonia, are then transferred to an absorber column in which they are contacted with additional amounts of water which separates the water soluble components of the gas (*e.g.*, acrylonitrile, HCN and acetonitrile) from the non-water soluble components (*e.g.*, N<sub>2</sub>, CO<sub>2</sub>, CO, propane, propylene) by absorption of the water soluble components in the aqueous phase. The liquid bottoms of this absorber column are then fed to a recovery column where the crude acrylonitrile and HCN are separated from the acetonitrile by distillation.

It is not uncommon for larger commercial acrylonitrile plants to include more than one (two, three or even more) separate ammoxidation reactors and the reactors share one or more common “back ends” for recovery and purification of the acrylonitrile, HCN and acetonitrile reaction products. In some of these plants, each ammoxidation reactor will have its own dedicated quench column, with the cooled reactor effluent gasses exiting these columns being transferred to a single common absorber column. In other of these plants, the hot reactor effluent gases passing out of the ammoxidation reactors are transferred to a common quench column.

The improved reactor startup procedure of this invention, as described above, can also be used in commercial acrylonitrile plants of this type too, by starting up the individual reactors separately, in series, with the proviso that the effluent gases from the second and subsequent reactors are not fed into the common backend equipment (*i.e.*, the common absorber column or the common quench column, as the case may be) until its oxygen concentration reduces to 8% or less, preferably 7% or less. Rather, the effluent gases from the second and subsequent reactors are vented, incinerated or otherwise discharged to waste until such time as their oxygen concentrations reduce down to these levels. In the alternative, a second and subsequent reactors may be started up with nitrogen gas (N<sub>2</sub>,) added to the second and subsequent reactors feed as a

diluent in such quantities so as to maintain the oxygen concentration in the effluent from the second and subsequent reactors at 8% or less, preferably 7% or less

In one aspect, a start-up process for an acrylonitrile reactor includes charging an ammoxidation catalyst into at least one ammoxidation reactor and heating the ammoxidation catalyst to at least a minimum ammonia oxidation temperature as described herein. The process further includes introducing ammonia and optionally propylene into the reactor in amounts effective for increasing catalyst temperature to an interim reaction temperature of about 415 °C to about 425 °C, wherein propylene is introduced into the reactor in an amount effective for preventing an unstable exothermic reaction. In this aspect, an interim reaction temperature of about 415 °C to about 425 °C is reached in about 5 hours or less after introduction of propylene to the reactor. An unstable exothermic reaction refers to a reaction where the temperature cannot be maintained in a range of about 415 °C to about 425 °C for a desired amount of time and uncontrollably goes above that range.

In another aspect, the process may further include introducing propylene into the reactor in an amount effective for increasing the interim catalyst temperature to a steady state reaction temperature of about 435 °C to about 445°C. In this aspect, a temperature of about 435 °C is reached at about 200 hours or more after introduction of propylene to the reactor, in another aspect, a temperature of about 440 °C is reached at about 250 hours or more after introduction of propylene to the reactor, and in another aspect, a temperature of about 435 °C to about 445°C is reached at about 1 to about 3 hours after introduction of propylene to the reactor.

#### Startup with Fresh Catalyst

A typical commercial ammoxidation reactor operates with the ammoxidation catalyst being maintained at a temperature of about 435° C to 445° C, *e.g.*, 440° C. Accordingly, when the acrylonitrile reactor being started up contains equilibrated catalyst, *i.e.*, ammoxidation catalyst that has already been used long enough so that its composition remains essentially constant over time, the reactor temperature is brought up to this level (about 435° C to 445° C) without delay. That is to say, once the ammoxidation reaction begins, the feed of propylene and ammonia to the ammoxidation catalyst are promptly increased to the levels required to achieve steady state operation at these temperatures, which typically takes about 1 to 3 hours.



However, fresh or new ammoxidation catalysts (i.e. catalysts which are not equilibrated catalysts) of the bismuth molybdate type when started up (i.e. exposed to reactor operating temperatures) are known to undergo a chemical change in that a portion of their molybdenum content is lost due to sublimation. While this phenomenon does not adversely affect the operation of the catalyst to any significant degree, the metallic molybdenum that sublimes off the catalyst normally condenses on the cooling coils of the ammoxidation reactor, which can lead to a variety of operational and equipment problems.

In accordance with another feature of this invention, the normal procedure used for starting up a commercial ammoxidation reactor which contains a new batch of a bismuth molybdate type ammoxidation catalyst is modified by delaying reaching the final steady state ammoxidation catalyst reaction temperature of about 435° C to 445° C for approximately two weeks or so. In accordance with this approach, the flowrates of propylene and ammonia to the ammoxidation catalyst are initially increased in a conventional manner for achieving a prompt increase in reaction temperature. However in this instance, this prompt increase in reaction temperature is interrupted when the ammoxidation catalyst reaches an interim reaction temperature of approximately 415° C to 425° C, *e.g.*, 420° C. At that time, the flowrates of propylene and ammonia are modified so that the temperature of the ammoxidation catalyst increases to its final steady state value of approximately 435° C to 445° C, *e.g.*, 440° C, only very gradually over a period of time of about two weeks or so, *i.e.*, over a period of time of about 275 to 400 hours, more commonly, about 325 to 350 hours. It has been found that this approach significantly reduces the rate at which molybdenum is released from the catalyst and hence the rate at which metal molybdenum condenses on the reactor cooling coils.

In another aspect, an interim reaction temperature of between about 415° C and about 425° C is reached within about 5 hours of the introduction of propylene to the reactor. In another aspect, the reaction temperature of between about 435° C and about 445° C is reached within about one to about 3 hours of the introduction of propylene to the reactor. In another aspect, when the interim reaction temperature is reached the propylene feed rate is gradually increased such that a reaction temperature of about 435° C or greater is reached at about 200 hours or more after the introduction of propylene to the reactor. In another aspect, a temperature of about 440° C or greater is reached at about 250 hours or more after the introduction of propylene to the reactor.

In another related aspect, an air to propylene molar ratio is maintained above a steady state air to propylene molar ratio for about 3 to about 96 hours after the introduction of propylene to the reactor, in another aspect, about 10 to about 90 hours, in another aspect, about 30 to about 70 hours, in another aspect, and about 40 to about 60 hours. In another aspect, the air to propylene molar ratio is maintained above the steady state air to propylene molar ratio for about 3 to about 96 hours, in another aspect, about 10 to about 90 hours, in another aspect, about 30 to about 70 hours, in another aspect, and about 40 to about 60 hours, after the introduction of propylene to the reactor at above a propylene to ammonia molar ratio of about 0.02

In another aspect, an ammonia breakthrough in the reactor effluent is maintained within a steady state ammonia breakthrough range after the introduction of propylene to the reactor at above a propylene to ammonia molar ratio of about 0.02. In this aspect, the steady state ammonia breakthrough range is about 6 about 9 molar % of ammonia feed. In another aspect, the ammonia to propylene molar ratio is maintained between about 0.05 and about 0.15 greater than the steady state ammonia to propylene molar ratio for about 3 to about 96 hours after the introduction of propylene to the reactor at above a propylene to ammonia molar ratio of about 0.02. In another related aspect, the reactor ammonia breakthrough is maintained based on the sulphuric acid feed rate necessary to maintain a constant pH in a quench system.

In another aspect, the reactor effluent is maintained within the steady state excess oxygen concentration range after the introduction of propylene to the reactor at above a propylene to ammonia molar ratio of about 0.02, wherein the steady state excess oxygen concentration range is about 0.5 to about 1.5 molar % .

In another aspect, an air to propylene molar ratio is maintained between about 0.5 and about 1.5 greater than the steady state air to propylene molar ratio until about 3 to about 96 hours after the introduction of propylene to the reactor at above a propylene to ammonia molar ratio of about 0.02. Reactor excess oxygen concentration may be maintained based on the measurement by a continuous on-line oxygen meter in the reactor effluent.

In another aspect, certain types of catalyst may need certain oxygen levels to prevent reduction. In this aspect, the oxygen concentration may be maintained between about 0.5 to about 7 volume % in the reactor effluent, in another aspect, about 0.5 to about 6 volume %, in another aspect, about 0.5 to about 5 volume %, in another aspect, about 0.5 to about 4 volume %, in another aspect,

in another aspect, about 0.5 to about 3 volume %, in another aspect, about 0.5 to about 2 volume %, and in another aspect, about 0.5 to about 1.5 volume %.

As can be seen from the foregoing description, the improved ammoxidation reactor start-up procedure of this invention provides a new approach to reactor start-up which not only achieves safer operation through better avoidance of explosive gas mixtures, especially in the reactor effluent gas, but also is very simple and inexpensive to operate.

Although only a few specific examples of this invention have been described above, it should be apparent that many modifications can be made without departing from the spirit and scope of this invention. All such modifications are intended to be included within the scope of this invention, which is to be limited only by the following claims.

## Claims:

1. In a process for starting up an acrylonitrile reactor containing a new charge of a bismuth molybdate ammoxidation catalyst, a method for reducing sublimation of molybdenum, the method comprising:

introducing propylene and ammonia to the reactor in an amount effective for increasing a temperature of the catalyst from an interim reaction temperature of about 415° C to about 425° C to a steady state reaction temperature of about 435° C to about 445° C over a period of time of about 1 to about 400 hours.

2. The process of claim 1 wherein the propylene feed rate is increased until a reaction temperature of between about 435° C and about 445° C is reached.

3. The process of claim 2 wherein an interim reaction temperature of between about 415° C and about 425° C is reached within about 5 hours of the introduction of propylene to the reactor.

4. The process of claim 3 wherein the reaction temperature of between about 435° C and about 445° C is reached within about one to about 3 hours of the introduction of propylene to the reactor.

5. The process of claim 2 wherein after the interim reaction temperature is reached the propylene feed rate is gradually increased such that a reaction temperature of about 435 ° C or greater is reached at about 200 hours or more after the introduction of propylene to the reactor.

6. The process of claim 2 wherein the reactor contains a new charge of charge of a bismuth molybdate ammoxidation catalyst and wherein a reaction temperature of about 440 ° C or greater is reached at about 250 hours or more after the introduction of propylene to the reactor.

7. The process of claim 1 wherein an air to propylene molar ratio is maintained above a steady state air to propylene molar ratio for about 3 to about 96 hours after the introduction of propylene to the reactor.

8. The process of claim 7 wherein the air to propylene molar ratio is maintained above the steady state air to propylene molar ratio for about 3 to about 96 hours after the introduction of propylene to the reactor at above a propylene to ammonia molar ratio of about 0.02

9. The process of claim 8 wherein the ammonia to propylene molar ratio is maintained above a steady state air to propylene molar ratio for about 3 to about 96 hours after the introduction of propylene to the reactor.

10. The process of claim 9 wherein the ammonia to propylene molar ratio is maintained above a steady state ammonia to propylene molar ratio for about 3 to about 96 hours after the introduction of propylene to the reactor at above a propylene to ammonia molar ratio of about 0.02.

11. The process of claim 1 wherein an ammonia breakthrough in the reactor effluent is maintained within a steady state ammonia breakthrough range after the introduction of propylene to the reactor at above a propylene to ammonia molar ratio of about 0.02.

12. The process of claim 11 wherein the steady state ammonia breakthrough range is about 6 about 9 molar % of ammonia feed.

13. The process of claim 10 wherein the ammonia to propylene molar ratio is maintained between about 0.05 and about 0.15 greater than the steady state ammonia to propylene molar ratio for about 3 to about 96 hours after the introduction of propylene to the reactor at above a propylene to ammonia molar ratio of about 0.02.

14. The process of claim 1 wherein the reactor ammonia breakthrough is maintained based on the sulphuric acid feed rate necessary to maintain a constant pH in a quench system.

15. The process of claim 1 wherein the in the reactor effluent is maintained within the steady state excess oxygen concentration range after the introduction of propylene to the reactor at above a propylene to ammonia molar ratio of about 0.02.

16. The process of claim 1 wherein the steady state excess oxygen concentration range is about 0.5 to about 1.5 molar % .

17. The process of claim 1 wherein an air to propylene molar ratio is maintained between about 0.5 and about 1.5 greater than the steady state air to propylene molar ratio until about 3 to about 96 hours after the introduction of propylene to the reactor at above a propylene to ammonia molar ratio of about 0.02.

18. The process of claim 17 wherein the reactor excess oxygen concentration is maintained based on the measurement by a continuous on-line oxygen meter in the reactor effluent.

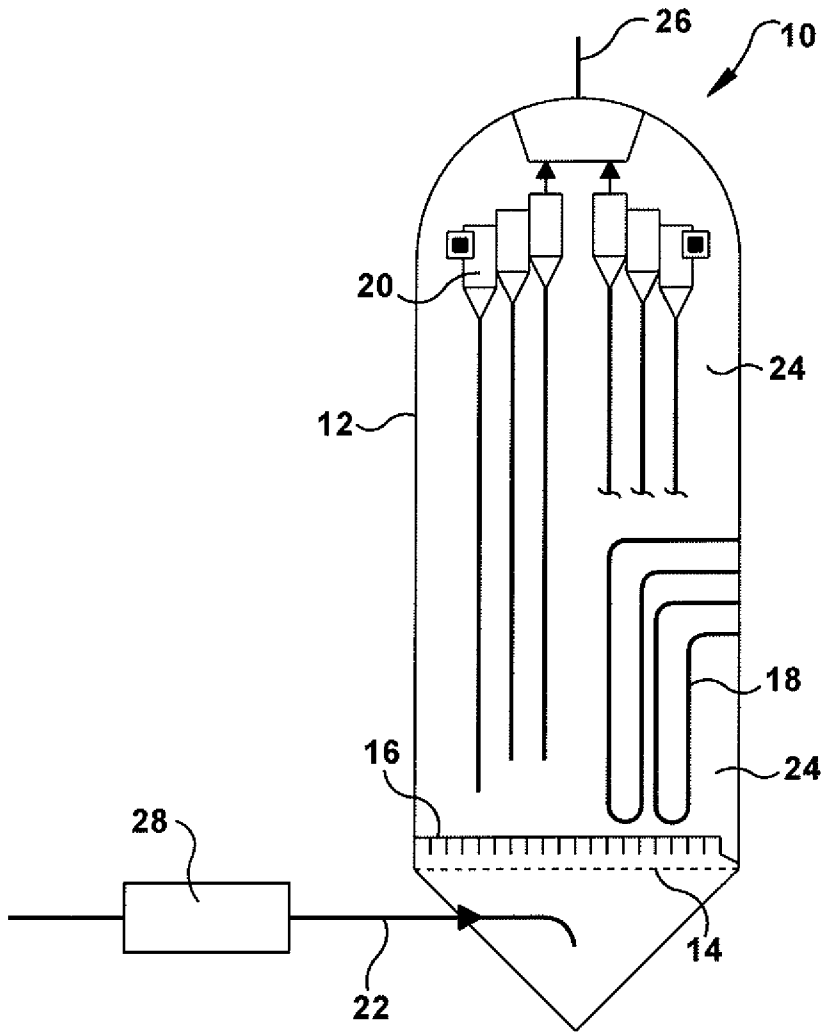


Fig. 1

INTERNATIONAL SEARCH REPORT

International application No  
PCT/US2014/023334

A. CLASSIFICATION OF SUBJECT MATTER  
INV. C07C253/26 C07C255/08  
ADD.  
According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED  
Minimum documentation searched (classification system followed by classification symbols)  
C07C  
Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)  
EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 4 228 098 A (AOKI KUNITOSHI ET AL) 14 October 1980 (1980-10-14) the whole document	1-18
A	----- US 3 766 092 A (HIRAKAWA K ET AL) 16 October 1973 (1973-10-16) the whole document -----	1-18

Further documents are listed in the continuation of Box C.

See patent family annex.

\* Special categories of cited documents :

- "A" document defining the general state of the art which is not considered to be of particular relevance
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# INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/US2014/023334

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