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(71) Applicant: **INVISTA TECHNOLOGIES S.À.R.L.**
 [LU/CH]; Zweigniederlassung St. Gallen, Kreuzacher-
 strasse 9, CH-9000 St. Gallen (CH).

(72) Inventors: **ROBINS, Clive, T.**; 10 Uplands Road, Dar-
 lington DL3 7SZ (GB). **CARRICK, Harald, B.**; The Old
 Free Church, Pleasance, Falkland, Cupar Fife KY15 7AN
 (GB). **AIRD, Graham**; 15 Dene Grove, Darlington DL3
 9LU (GB).

(74) Agent: **MACKENZIE, Stephen, J.**; Three Little Falls
 Centre, 2801 Centerville Road, Wilmington, DE 19808
 (US).

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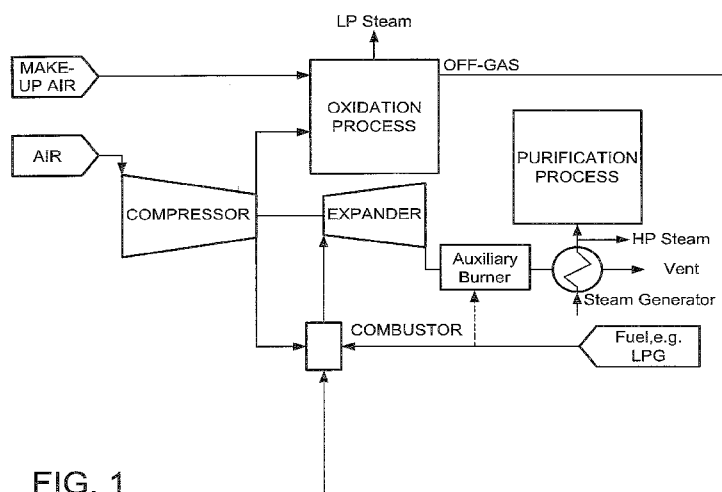


FIG. 1

(57) Abstract: The invention relates to a method and system for recovering power from the gaseous stream produced by a paraxylene - air oxidation reaction. Specifically, the invention is based on heating the gaseous stream from the oxidation reaction to a temperature of at least 600°C, recovering energy through an expander, heating the expander vent stream and recovering heat from the vent stream. The recovered heat is used to maintain the oxidation process, purification process, start-up the process, or re-start the process after an interruption.

POWER RECOVERY FOR USE IN START-UP OR RE-START OF A PURE TEREPHTHALIC ACID PRODUCTION PROCESS

RELATED APPLICATIONS

[0001] This application is a PCT of U.S. Application Serial No. 13/901666, filed on May 24, 2013 which in turn is a continuation-in-part of application Serial No. 12/990,984, entitled "Power Recovery", filed on December 7, 2010, which claims priority to U.S. Provisional Application Serial No. 61/108,233, filed on October 24, 2008, the disclosures of which are incorporated herein by reference in their entirety.

FIELD OF THE INVENTION

[0002] This invention relates to a method for recovering power from the gaseous stream ("off-gas") produced by an oxidation reaction, for example the oxidations of para-xylene (pX) to terephthalic acid (TA) and dimethyl terephthalate (DMT) or of cyclohexane to cyclohexanone / cyclohexanol. Specifically disclosed herein is an oxidation reaction system comprising a power recovery system and a method for the recovery of energy as a high grade heat source such as high pressure steam, hot oil or the like, for use in starting, running or re-starting a PTA production process.

BACKGROUND OF THE INVENTION

[0003] Many industrial synthetic chemical processes, for example the synthetic oxidation of para-xylene (pX) to terephthalic acid (TA), and destructive chemical processes, for example the oxidation of organic waste, occur at high temperatures and pressures. The production of TA, for example, typically involves the liquid phase oxidation of pX feedstock using molecular oxygen in acetic acid, in the presence of a

dissolved heavy metal catalyst system usually incorporating a promoter, such as bromine as disclosed in US patent number 2,833,816. In general, acetic acid, molecular oxygen in the form of air, para-xylene and catalyst are fed continuously into the oxidation reactor at elevated temperature and pressure, typically a temperature from about 150°C to about 250°C and a pressure from about 600 kPa to about 2500 kPa.

[0004] Para-xylene oxidation produces a high-pressure gaseous stream (or “off-gas”) which comprises nitrogen, unreacted oxygen, carbon dioxide, carbon monoxide and, where bromine is used as a promoter, methyl bromide. In addition, because the reaction is exothermic, the acetic acid solvent is frequently allowed to vaporize to control the reaction temperature and is removed in the gaseous stream. This vapour is typically condensed and most of the condensate is refluxed to the reactor, with some condensate being withdrawn to control reactor water concentration. The portion of the gaseous stream which is not condensed is either vented, or passed through a catalytic combustion unit (CCU) to form an environmentally acceptable effluent as disclosed in publication WO 96/39595. Catalytic combustors have been deployed on TA plants typically upstream of an expander. Their function is to catalytically combust volatile organic compounds (VOC's) and carbon monoxide.

[0005] The gaseous stream from the reactor contains a significant amount of energy. This energy can be recovered to offset, at least partially, the cost of obtaining the high temperatures and pressures required in the oxidation reactor. For example, WO 96/11899 and JP 8-155265 disclose directing the high pressure gaseous stream to a means for recovering energy, for example an expander, which is connected to an electric generator or other equipment requiring mechanical work,

such as a compressor. Power recovery using an expander (for example as disclosed in WO 96/39595) is conventionally carried out at temperatures from about 150-750 °C, typically 450°C. However, there is scope to improve power recovery using an expander by changes to the configuration of the manufacturing process and the means for recovering power from the process, for example as disclosed in API 616 Gas Turbines for the Petroleum, Chemical and Gas Industry Services.

[0006] The TA manufacturing process requires a source of heat above 300°C to heat the feed stream to the Purification plant hydrogenation reactor. This duty is typically accomplished using a source of High Pressure (HP) Steam (for example at about 100 bara, 311°C) or hot oil at similar or even higher temperatures. Normally, HP steam for this purpose is imported from a Utility provider or raised on site following installation of a packaged boiler assembly.

[0007] Similarly, some power for the PTA process is typically provided by a utility provider.

SUMMARY OF THE INVENTION

[0008] There is a desire for improved power and energy recovery systems that can improve the overall cost-effectiveness of the PTA production process. Improvements have been made to the energy efficiency of the PTA production process, however, the improvements comprise multiple and separate systems, adding additional complexity to the normal operation of the production process. Further, additional sources of high grade heat are required to start-up the production process or when the oxidation reactor is not in normal operation, such as an unplanned process interruption or stop ("Trip").

[0009] The invention disclosed herein provides for improved processes for the production of PTA, and specifically to modifications of the operation of Internal Combustion Open Cycle Gas Turbines ICOCGTs to improve the thermodynamic efficiency of the terephthalic acid purification step of the PTA production process. As disclosed herein, the process generates high grade heat while eliminating the requirement for separate sources of high temperature heat or the provision of a high grade heat source utility system for the PTA production process.

[0010] In one aspect, a process for recovering power from a paraxylene - air oxidation reaction to produce terephthalic acid, where the oxidation reaction produces a gaseous stream is disclosed. The process comprises: (a) heating the gaseous stream to a temperature of at least 600°C; (b) sending the gaseous stream to an expander that drives a compressor, wherein the compressor compresses air which is fed to the oxidation reactor and the expander emits a gaseous vent stream; (c) feeding the gaseous vent stream to a heat recovery system to produce recovered heat; and (d) generating high grade heat from the recovered heat. The expander can drive the compressor via a shaft that couples the two together. The heat recovery system can be a heat exchanger or a combustor feed interchanger. The high grade heat can be high pressure steam or hot oil. The high grade heat generated can be used, for example, when the oxidation reactor operation is interrupted or experiences a process upset ("Trip") (which prevents the generation and reuse of energy from the process itself) to maintain the terephthalic acid purification stage and subsequently to restart the oxidation reactor.

[0011] In another aspect, a paraxylene - air oxidation reaction to produce terephthalic acid system is disclosed. The system comprises: (a) an oxidation reactor comprising an oxidant inlet and a gaseous stream outlet, wherein the reactor

emits a gaseous stream from the gaseous stream outlet; (b) a power recovery system connected to the gaseous stream outlet comprising: (i) a heater for receiving and heating the gaseous stream connected downstream of the gaseous stream outlet; and (ii) an expander positioned downstream of the heater that drives a compressor, wherein the compressor produces a compressed air stream and the expander emits a gaseous vent stream; and (c) a heat recovery system for receiving the gaseous vent stream and producing a high grade heat stream. The heat recovery system can be a heat exchanger or a combustor feed interchanger. The expander can drive the compressor via a shaft that couples the two together. The heat stream can be used, for example, when the oxidation reactor operation is interrupted or experiences a process upset ("Trip") (which prevents the generation and reuse of energy from the process itself) to maintain the terephthalic acid purification stage and subsequently to restart the oxidation reactor.

[00012] In yet a further aspect, a process for maintaining the operation of a terephthalic acid oxidation plant during a process interruption is disclosed. The process comprises: (a) retaining a concentration of oxygen in a first combustor sufficient to sustain combustion and generate a combusted gas stream; (b) feeding the combusted gas stream to an expander, which produces a vent gas stream; (c) feeding the vent gas stream to a heat recovery system, with an optional auxiliary combustor, to produce recovered heat; and (d) using the recovered heat to maintain the operation of the terephthalic acid oxidation plant duties. The recovered heat can be high pressure steam or hot oil. The recovered heat can be used in the terephthalic acid purification stage, oxidation stage to start-up an oxidation reaction, re-start an oxidation reaction, or a combination.

DEFINITIONS

[00013] Gaseous stream: gas stream produced from an oxidation reaction.

[00014] Gaseous vent stream: gas stream that emits from an expander.

BRIEF DESCRIPTION OF DRAWINGS

[00015] The figures describe examples of the different aspects (configurations and modes) of the present invention.

[00016] Figure 1 is a schematic diagram of one aspect of the process.

[00017] Figure 2 is a schematic diagram that illustrates an interrupted oxidation reaction where the compressed air by-passes the oxidation reactor and is fed directly to the combustion chamber and expander.

[00018] In any of these configurations a generator can be attached to the expander. The net power generated can be used to offset the power requirement of the PTA plant. Surplus power can be exported from the plant.

DETAILED DESCRIPTION OF THE INVENTION

[00019] The present invention can be characterized by a process for recovering power from an oxidation reaction that produces a gaseous stream. The process comprises: (a) heating the gaseous stream to a temperature of at least 600°C; (b) sending the gaseous stream to an expander that drives a compressor, wherein the compressor compresses air which is fed to the reactor and the expander emits a gaseous vent stream; (c) feeding the gaseous vent stream to a heat recovery system to produce recovered heat; and (d) generating high grade heat from the recovered heat. The high grade heat can be used in part at least to heat high temperature process streams in the process plant.

[00020] In the case of terephthalic acid (TA), air is fed to an oxidation reactor wherein paraxylene is oxidized to terephthalic acid in a reaction whose liquor comprises acetic acid, paraxylene, cobalt acetate, manganese acetate and hydrogen bromide where the crude terephthalic acid is generated as a solid in the reaction slurry. The slurry is typically cooled in a series of crystallisers and then isolated by solid-liquid using a suitable device such as a rotary drum filter, a belt filter or a centrifuge. The acetic acid-wet TA cake is then optionally either dried to form a dry crude terephthalic acid or is washed using water to create a water-wet TA cake. The resulting dry or water-wet cake is slurried in water and heated to sufficient temperature to dissolve the (relatively insoluble) TA in water. This is typically done industrially at a temperature of above 230 degrees C.

[00021] The high grade heat generated from the use of the gas turbine can be used to heat high temperature streams in a terephthalic acid purification process and TA oxidation process where temperatures of $>230^{\circ}\text{C}$ are required. The expander can drive the compressor via a shaft that couples the two together. The heat recovery system can be a heat exchanger or a combustor feed interchanger. The high grade heat can be high pressure steam or hot oil. Optionally, an auxiliary combustor can be used to heat the gaseous vent stream prior to feeding the stream to a heat recovery system.

[00022] The high grade heat can also be used to heat high temperature streams to maintain the terephthalic acid purification stage and subsequently to restart the oxidation reactor when the oxidation reactor operation is interrupted or experiences a process upset ("Trip") which prevents the generation and reuse of energy from the process itself. Here, sufficient high pressure steam or hot oil can continue to be supplied to the production process, even if the oxidation reaction exotherm is not

recovered. For example, steam raised by the combustor can be used, when the oxidation reactor operation is interrupted or experiences a process upset, to maintain the terephthalic acid purification state in operation and subsequently to restart the oxidation stage of the production process.

Optimizing the Operation of the ICOCGT

[00023] To optimize the operation of the ICOCGT, it can be important to boost the gaseous stream pressure using an additional booster compressor. This booster compressor can be either upstream of the oxidation reactor if the ICOCGT compressor discharges at a pressure lower than the oxidation reaction pressure, or downstream if the ICOCGT compressor discharges at a higher pressure than the oxidation reaction pressure.

[00024] To optimize the operation of the ICOCGT, it can be important to inject gas to the gaseous stream from the oxidation reactor. This can be done by injecting water, steam, air or some other suitable available gas. Air can be provided from a make-up air compressor. This make-up air supplements the compressed air available from the ICOCGT compressor and also ensures adequate oxygen in the ICOCGT combustor.

Generation and Heating of the gaseous stream

[00025] Prior to heating the gaseous stream or mixing the gaseous stream with make-up gas (water, steam, air or other gas), solvent in the gaseous stream (for example acetic acid in TA production) can be condensed to avoid yield loss, for example using separation apparatus such as a distillation column or overhead condensers. For paraxylene (pX) – air oxidation processes, usually most of the condensate is refluxed to the reactor, with some of the condensate being withdrawn to control reactor water concentration (two moles of water are formed per mole of pX

reacted in TA production). For pX – air oxidation process to TA, when it leaves the reactor, the gaseous stream typically has a temperature from 150 to 220°C and a pressure from 600 kPa to 2500 kPa. The temperature and pressure of the reactor can be selected to optimize the operation of the reactor and the downstream processes. Different temperatures apply for other processes.

[00026] The gaseous stream leaving the reactor is heated to at least 600°C with any suitable heater or combination of heaters. Examples of these might be a process heat exchanger heated by available hot utility source (such as steam or hot oil) or an available hot process stream, a direct heater of the gaseous stream (such as a combustor fuelled for example with natural gas or fuel oil), or an indirect heater of the gaseous stream (such as a furnace fuelled for example with natural gas or fuel oil). In one embodiment, fuel and oxidant (for example from the reactor oxidant feed) are mixed with the gaseous stream in a combustor and burnt in order to raise the temperature of the gaseous stream directly. In another embodiment, a furnace heats the gaseous stream indirectly, *i.e.* fuel and oxidant (for example air) are burnt in the furnace without mixing with the gaseous stream and the gaseous stream is heated by indirect heat exchange as it passes through the furnace. Indirect heating can be advantageous as it does not require additional oxidant to be fed above atmospheric pressure to the gaseous stream to burn the fuel. Instead indirect heating can involve combustion of fuel using atmospheric air.

[00027] Optionally, other auxiliary heaters can be used in addition to the heater for heating the gaseous stream. Prior to heating (*i.e.* upstream of the heater), the gaseous stream can be fed to a catalytic combustion unit (CCU). CCUs are typically used for environmental reasons to remove organic compounds and reactor by-products in the gaseous stream and operate by flameless oxidation of the organic

compounds *etc.* (e.g. MeBr). Typically, the gaseous stream leaving the CCU has a temperature of from about 350°C to about 600°C. Optionally, the gaseous stream can be heated with an interchanger, *i.e.* a heat exchanger that transfers heat between a process stream and the gaseous stream.

[00028] The temperature of the gaseous stream entering the CCU can be about 250°C to about 400°C, for example about 300°C, to ensure stable combustion in the CCU. Prior to treatment with the CCU, the gaseous stream can be heated from about 200°C to about 350°C, for example from about 300°C to about 350°C. A steam heater provided upstream of the CCU can be used to achieve such heating. The steam heater can use steam produced as a by-product of the oxidation reaction to heat the gaseous stream.

[00029] Following the CCU, optionally the gas can be treated, for example by scrubbing (for example by use of a scrubber), to remove reactive components such as HBr and Br₂ prior to feeding to a gas heater. One way of heating the gaseous feed stream to the CCU can be to interchange heat with the CCU exit stream.

Addition of Air

[00030] Air can also be added to the gaseous stream or the compressed air stream to increase the oxygen concentration of the mixed air / catalytically combusted gaseous stream to the combustion chamber of the ICOCGT or else added directly to the combustor. The gaseous stream, immediately prior to entering the expander (stream 9) has a temperature of at least 600°C, including from about 600°C to 1400°C, from 600°C to about 1100°C, from 800°C to about 1100°C, 900°C, 950°C, 1000°C, and 1050°C. Air can be added to the gaseous stream to compensate for the oxygen consumed in the oxidation reactor and offgas (gaseous

stream from the oxidation reactor) used in other ways (for example product powder conveying), and to ensure sufficient oxygen is available for combustion of the catalytically combusted gaseous stream (stream 8). The mass flow of added air can be in the range of from about 0% to about 35% of the mass flow of the compressed air to the reactor, for example during normal operation about 20% , of the mass flow of the compressed air to the reactor.

[00031] Air compression is a costly step in the reaction process, therefore, this cost should be partially offset by power recovery from the gaseous stream. Also, under some circumstances the temperature of the compressed air stream can be excessively high to be fed directly to the oxidation reactor and can be used as a heating medium, for example, to displace the use of steam and thereby improving the overall energy efficiency of the production process. To minimize the capital cost of the power recovery system, the gas turbine used in the disclosed processes can be of a standard design and construction (as stated above) with only minor modifications. Generally, the disclosed processes use a gas turbine designed for the temperatures, pressures, and flow rates of the gaseous stream, and that needed for compressing the air fed to the reactor. Optionally, an additional compressor or booster can be used before the compressed air inlet to the reactor or to increase the pressure of the gaseous stream. Multiple gas turbines can be used in parallel to optimize the compressed air flow rates to match the PTA production plant capacity. Further, a heater (indirect or direct) can be provided to heat the air.

The gas turbine

[00032] As used herein, a "gas turbine" refers to a standard gas turbine, for example those described and listed in API 616 Gas Turbines for the Petroleum,

Chemical and Gas Industry Services and Turbomachinery International Handbook 2006, vol. 46, no. 6, comprising a compressor coupled to an expander by one or more shafts. The expander is connected to the gaseous stream downstream of the heater. The compressor is connected to the oxidant inlet of the reactor and compresses the gaseous oxidant fed to the reactor. Typically, the expander power generated will be greater than the compressor power consumption.

[00033] Because compressing the oxidant (which is used in significant quantities in the reactor) is a costly step in the reaction process, it is advantageous that this cost be at least partially offset by power recovery from the gaseous stream.

[00034] To minimise the capital cost of the power recovery system, the gas turbine used in the invention can be of a standard design and construction with only minor modification. Generally, the present invention selects a gas turbine designed for the temperatures, pressures and flow rates of the gaseous stream, and the power requirements of the compressor for compressing the oxidant feed. An expander or booster compressor can be provided downstream of the gas turbine compressor on the gaseous oxidant feed. This expander or compressor allows adjustment of the gas turbine's compressor discharge to match the optimum pressure of gaseous oxidant into the reactor in order to assist with the integration of the gas turbine with the remaining components of the power recovery system and the reactor, and to allow optimisation of the power recovery. This embodiment can be particularly advantageous, as it enables de-coupling of the requirements of the gas turbine and reactor, thereby allowing the reactor and gas turbine operations to be optimised independently. Alternatively, a booster compressor can be located downstream of the oxidation reactor and upstream of the heater to adjust and optimise the pressure of the gaseous stream into the expander.

[00035] Gas (for example steam or air) can be added to the gaseous stream, prior to, or simultaneously with, feeding the gaseous stream to the expander inlet. In one embodiment, gas can be added to the gaseous stream prior to feeding the gaseous stream to the expander inlet (*i.e.* upstream of the expander) and, therefore, in the power recovery system of the invention, the steam (or air) inlet is upstream of the expander. This can be advantageous to match the compressor and expander duties, enabling the use of a standard gas turbine.

[00036] Alternatively air can be added to the compressed air stream from the ICOCGT to provide the matching of compressor and expander duties. This arrangement reduces the amount of compressed air that needs to be extracted from the ICOCGT compressor and returned externally to the ICOCGT combustor.

[00037] An Internal Combustion Open Cycle Gas Turbine (ICOCGT), as disclosed in API 616 Gas Turbines for the Petroleum, Chemical and Gas Industry Services, comprises a compressor, a combustor and an expander and is optimized to generate power. An embodiment of the present invention utilizes an ICOCGT to beneficially recover power from the gaseous stream produced by an oxidation reaction.

[00038] The compressor stage of the ICOCGT compresses the oxidant feed to the reactor (at greater than atmospheric pressure) thereby at least partially offsetting the cost of providing the high temperature and pressure reaction conditions in the reactor.

[00039] The expander stage of the ICOCGT expands the heated gaseous stream from the oxidation reactor recovering energy to power the compressor and a hot gas stream, for example to raise steam downstream of the ICOCGT. The net power

generated can be used to offset the power requirement of the PTA plant. Surplus power can be exported from the plant.

Oxidation Reactor

[00040] The reactor is a continuous flow reactor, meaning a reactor in which reactants are introduced and mixed and products withdrawn simultaneously in a continuous manner, as opposed to a batch-type reactor. In this invention a standard oxidation reactor, for example as disclosed in US 7,153,480, can be used. Standard reactants and operating conditions, for example as disclosed in US 7,153,480, can also be used.

[00041] The invention is suitable for any oxidation reaction producing a gaseous stream, *i.e.* gaseous reaction products. For example, oxidation reactions include cyclohexane oxidation, pX - air oxidation to TA or dimethyl terephthalate, metaxylene oxidation to isophthalic acid *etc.* However, the air oxidation of pX to TA is of particular interest in the invention.

[00042] The oxidant in the invention can be molecular oxygen, for example air (including oxygen-depleted air and oxygen enriched air).

[00043] Oxidation reactions are typically exothermic and heat can be removed, in order to control the reaction temperature, by removing the volatile components, condensing them, and returning the condensate to the reactor. Alternatively or additionally, the heat of reaction can be removed from the reaction by heat exchange with a heat-accepting fluid, according to conventional techniques known to those skilled in the art.

[00044] As mentioned above, the reactor is generally operated in a continuous mode. By carrying out the process in a continuous flow reactor, the residence time for the reaction can be made compatible with the attainment of conversion of the precursors to the desired product without significant production of degradation products.

[00045] The gaseous stream can be heated to a temperature to at least 600°C, including from about 600°C to 1400°C, from 600°C to about 1100°C, from 800°C to about 1100°C, 900°C, 950°C, 1000°C, and 1050°C

[00046] As used herein, reference to the production of a carboxylic acid includes reference to the production of its ester. As will be evident to the skilled person, whether a carboxylic acid or its ester is produced will depend on the conditions in the reactor and/or the conditions used to purify the products.

[00047] As used herein, "aromatic carboxylic acid precursor" or "precursor" means an organic compound, preferably a hydrocarbon, capable of being oxidised to a specific aromatic carboxylic acid in a majority yield in the presence of selective oxidising conditions. An example of a terephthalic acid precursor is paraxylene. An example of an isophthalic acid precursor is metaxylene.

[00048] The disclosed processes can comprise feeding solvent, oxidant, precursor and catalyst into an oxidation reactor that is maintained at a temperature in the range of from about 150°C to about 250°C, for example about 175°C to about 225°C, and a pressure in the range of from about 100 kPa to about 5000 kPa, for example about 1000 kPa to about 3000 kPa.

[00049] The oxidation reaction can be carried out in the presence of an oxidation catalyst. The catalyst can be substantially soluble in the reaction medium comprising

solvent and the aromatic carboxylic acid precursor(s). The catalyst can comprise one or more heavy metal compounds, for example cobalt and/or manganese compounds, and can optionally include an oxidation promoter. For instance, the catalyst can take any of the forms that have been used in the liquid phase oxidation of aromatic carboxylic acid precursors such as terephthalic acid precursor(s) in aliphatic aromatic carboxylic acid solvent, for example bromides, bromoalkanoates or alkanoates (usually C₁-C₄ alkanoates such as acetates) of cobalt and/or manganese. Compounds of other heavy metals such as vanadium, chromium, iron, molybdenum, a lanthanide such as cerium, zirconium, hafnium, and/or nickel can be used instead of, or additional to, cobalt and/or manganese. Advantageously, the catalyst system can include manganese bromide (MnBr₂) and/or cobalt bromide (CoBr₂). The oxidation promoter, where employed, can be in the form of elemental bromine, ionic bromide (for example HBr, NaBr, KBr, NH₄Br) and/or organic bromide (for example bromobenzenes, benzyl-bromide, mono- and di-bromoacetic acid, bromoacetyl bromide, tetrabromoethane, ethylene-di-bromide, *etc.*).

[00050] Any suitable solvent in which the oxidation reaction can take place can be used. Where the oxidation reaction is the catalytic liquid phase oxidation of a precursor to produce aromatic carboxylic acid, the solvent can be an aliphatic monocarboxylic acid having from 2 to 6 carbon atoms, for example, the solvent can be acetic acid. Acetic acid can be particularly useful as the solvent since it is relatively resistant to oxidation in comparison with other solvents and increases the activity of the catalytic pathway.

[00051] The reaction can be effected by heating and pressurising the precursor, catalyst and solvent mixture followed by introduction of the oxidant into the reactor via the oxidant inlet.

[00052] The effluent, *i.e.* reaction product, from the oxidation reactor can be a slurry of aromatic carboxylic acid crystals which are recovered from the slurry by filtration and subsequent washing. They can thereafter be fed to a separate terephthalic acid purification step or directly to a polymerization process, for example, the main impurity in crude TPA is 4-carboxybenzaldehyde (4-CBA), which is incompletely oxidized paraxylene, although other oxidation products and precursors to terephthalic acid such as p-tolualdehyde and p-toluic acid can also be present as contaminants.

Reactor Trip and Re-start

[00053] Disclosed in Figure 2 is one aspect of a process for maintaining the operation of a TA oxidation plant during a process interruption. During a process upset or interruption of the oxidation process, the compressed air stream is isolated from the oxidation reactor and diverted directly to the combustion chamber and then fed to the gas turbine expander. As a result, no gaseous stream flows from the oxidation reactor to the condenser. The catalytic combustor can also optionally be isolated in this scenario. Alternatively, the compressed air stream can flow through the catalytic combustor to the combustion chamber, followed by an optional and a small flow or no make-up air flow to the combustion chamber. This change separates the operation of the oxidation reactor and the gas turbine. The gas turbine continues to operate, producing steam in the steam generator, enabling other stages of the process to continue in operation.

[00054] For interrupted operation, no air is fed to the oxidation reactor and compressed air flows via a bypass to the combustion chamber, where it is mixed with fuel and combusted, as per operation of an ICOCGT in a more typical

configuration. The concentration of oxygen in the compressed air fed to the combustion chamber is the same as ambient air and no make-up air is required (to compensate for oxygen consumed). The compression duty is the same as for routine operation, but in this configuration all of the compressed air flows to the combustion chamber. The vent stream from the expander flows to the steam generator where high pressure steam is raised to maintain operation of the rest of the PTA production process. However, additional heating is required in the auxiliary combustor to generate the required steam demand in the absence of oxidation exotherm being recovered from the oxidation reactor. The difference is made up by burning additional fuel in the auxiliary combustor.

[00055] Surprisingly, controlling the operation of the ICOCGT increases output of high grade heat, such as high pressure steam from the steam generator. This increase is achieved by retaining oxygen in the ICOCGT sufficient to sustain combustion and feeding the vent gas stream (still containing the oxygen not consumed in the oxidation reactor) from the expander to an auxiliary combustor together with more fuel. The increased heat output, in the absence of heat from the oxidation reactor, can be designed to be sufficient to keep the terephthalic acid purification stage in routine operation, start-up the oxidation stage of the process after a process interruption and supply other process uses, thereby eliminating the need for other sources of high grade heat, such as high pressure steam. With high pressure steam, as the steam generator operates continuously when the oxidation stage of the production process is in operation, its change of duty to generate steam when the oxidation reactor operation is interrupted can be handled very rapidly, enabling the reset of the production stages to remain in routine operation. Consequently, the cause of the oxidation process upset or interruption can be

investigated in isolation of the rest of the production process and reducing the impact on output from the production plant.

[00056] Also disclosed are systems that utilize various aspects of the disclosed methods. In one aspect, the system comprises: (a) an oxidation reactor comprising an oxidant inlet and a gaseous stream outlet, wherein said reactor emits a gaseous stream from said gaseous stream outlet; (b) a power recovery system connected to the gaseous outlet comprising: (i) a heater for receiving and heating the gaseous stream connected downstream of the gaseous stream outlet; and (ii) a gas turbine expander positioned downstream of the heater that drives a compressor, wherein the compressor produces a compressed air stream and the expander emits a gaseous vent stream; and (c) a heat recovery system for receiving the gaseous vent stream and producing a high grade heat stream. Optionally, an auxiliary combustor for receiving the gaseous vent stream and producing a heated gaseous vent stream is placed prior to the heat recovery system.

[00057] The heat recovery system can be a heat exchanger or a combustor feed interchanger. The power recovery system comprises an expander that drives a compressor. The expander can drive the compressor via a shaft that couples the two together. The system that utilizes the expander vent gas can be employed in situations where process interruptions occur. Here, the heat recovered from the heated vent stream is sufficient enough to generate high pressure steam or hot oil for use in the terephthalic acid purification stage, the paraxylene – air oxidation stage, start-up, re-starting of the process, or a combination.

Examples

[00058] The following examples further illustrate the various aspects of the disclosed processes and systems. The mass and heat balances have been calculated based on the schematics shown in Figure 1 for normal operation and Figure 2 for interrupted operation, but other aspects show similar results.

[00059] Table 1 (below) assumes the use of high pressure ("HP") steam and shows the relative mass flows, compared to the normal generation of high pressure steam, for the two modes of operation. For normal operation, ambient air is compressed and heated to about 365°C before flowing to the combustor feed interchanger, where it is cooled, before feeding to the oxidation reactor. The gaseous stream vented from the oxidation reactor flows to a condenser to remove condensables, before the gaseous stream temperature is increased in the combustor feed interchanger and heater. The heated gaseous stream flows to the catalytic combustor, where volatile organics and other gaseous components are combusted. The combusted gaseous stream flows to the combustion chamber at the inlet to the expander. Fuel is only fed to this combustion chamber, with make-up air raising the oxygen concentration above the threshold for stable combustion, typically around 14-17% w/w. The vent stream from the expander flows to the steam generator where HP steam is raised for routine use on the PTA production process. No additional heating is required in the auxiliary combustor to generate the base-load high pressure steam demand.

[00060] Table 1 – relative stream flows and temperatures

Example		HP steam generated	Comp. Air	Make up air	Fuel to combust	Fuel to aux. combust	Gas to expander	Vent gas from steam gen
Normal Op.	Relative mass flow	1	6.25	1.1	0.095	0	6.63	6.63
	Temp	310°C	365°C	385°C	-	-	950°C - 1050°C	180°C
Interrupted Op. of reactor	Relative mass flow	2.3	6.25	0.07	0.096	0.085	6.43	6.52
	Temp	310°C	365°C	385°C	-	-	950°C – 1050°C	120°C

CLAIMS

We claim:

1. A process for generating and recovering power from a paraxylene – air oxidation reaction to produce terephthalic acid utilising an internal combustion open cycle gas turbine (ICOCGT) which includes a compressor, combustor and expander, wherein the oxidation reaction produces a gaseous stream. comprising:
 - a. heating the gaseous stream to a temperature of at least 600°C;
 - b. sending the gaseous stream to an ICOCGT expander that drives an ICOCGT compressor, wherein the compressor compresses air fed to the oxidation reactor and the expander emits a gaseous vent stream;
 - c. feeding the gaseous vent stream to a heat recovery system to produce recovered heat; and
 - d. generating high grade heat from the recovered heat.
2. The process of claim 1, wherein the heat recovery system comprises a heat exchanger or a combustor feed interchanger.
3. The process of claim 1, wherein said heating is achieved in the ICOCGT combustor.
4. The process of claim 1, further comprising feeding the gaseous stream to a catalytic combustion unit prior to heating to at least 600°C.
5. The process of claim 4, wherein the catalytic combustion unit heats the gaseous stream to a temperature between about 300°C to about 600°C.
6. The process of claim 4 wherein a fuel stream is fed to the ICOCGT combustor.

7. The process of claim 1, wherein the gaseous stream is mixed with a compressed air stream prior to said heating.
8. The process of claim 1, wherein make-up air is added to the compressed air stream in order to balance ICOCGT compressor and ICOCGT expander flows.
9. The process of claim 1, wherein the gaseous stream contacts at least one condenser to substantially remove condensables prior to heating.
10. The process of claim 9, wherein the condensables comprise acetic acid.
11. The process of claim 1, wherein the gaseous vent stream is fed to an auxiliary combustor to produce a heated gaseous vent stream, and the heated gaseous vent stream is fed to the heat recovery system.
12. The process of claim 11, wherein a fuel stream is fed to the auxiliary combustor.
13. The process of claim 1, wherein the high grade heat is recovered as high pressure steam or hot oil, which is used to heat a terephthalic acid purification stage.
14. The process of claim 1, wherein at least a portion of the high grade heat is used in a paraxylene - air oxidation reaction stage.
15. The process of claim 1, wherein the pressure of the air fed to the reactor is boosted by a second compressor.

16. The process of claim 1, wherein the pressure of the gaseous stream is boosted by a second compressor prior to feeding to the ICOCGT expander.
17. A paraxylene - air oxidation reaction to produce terephthalic acid system, utilising an internal combustion open cycle gas turbine (ICOCGT) which includes a compressor, combustor and expander, comprising:
- a. an oxidation reactor comprising an oxidant inlet and a gaseous stream outlet, wherein said reactor emits a gaseous stream from said gaseous stream outlet;
 - b. a power recovery system connected to the gaseous stream outlet comprising: (i) a heater for receiving and heating the gaseous stream connected downstream of the gaseous stream outlet; and (ii) an ICOCGT expander positioned downstream of the heater that drives an ICOCGT compressor, wherein the compressor produces a compressed air stream and the expander emits a gaseous vent stream; and
 - c. a heat recovery system for receiving the gaseous vent stream and producing a high grade heat stream.
18. The system of claim 17, wherein the heat recovery system comprises a heat exchanger and optionally an auxiliary combustor.
19. The system of claim 17, wherein the heater comprises a combustor.
20. The system of claim 17, further comprising a catalytic combustion unit upstream of said heater.
21. The system of claim 16, wherein the catalytic combustion unit heats the gaseous stream to a temperature between about 300°C and about 600°C.

22. The system of claim 19, wherein the combustor has a fuel stream inlet.
23. The system of claim 17, wherein the gaseous stream is mixed with a compressed air stream prior to entering said heater.
24. The system of claim 17, wherein make-up air is added to the compressed air stream in order to balance ICOCGT compressor and ICOCGT expander flows.
25. The system of claim 17, wherein the gaseous stream is substantially devoid of condensables prior to entering said heater.
26. The system of claim 25, wherein the condensables comprise acetic acid.
27. The system of claim 18, wherein the auxiliary combustor has a fuel stream inlet.
28. The system of claim 17, further comprising a steam generator for receiving the high grade heat stream and producing high pressure steam.
29. The system of claim 28, wherein the high pressure steam is used in a terephthalic acid purification stage.
30. The system of claim 17, wherein at least a portion of the high grade heat stream is used in a paraxylene - air oxidation stage.
31. The system of claim 17, further comprising a hot oil generator for receiving the high grade heat stream and producing hot oil.

32. The system of claim 31, wherein the hot oil is used in a terephthalic acid purification stage.
33. The system of claim 17, further comprising a second compressor connected to the oxidant inlet.
34. The system of claim 17, further comprising a second compressor connected to the gaseous stream outlet prior to the ICOCGT expander.
35. A process, utilising an internal combustion open cycle gas turbine (ICOCGT) which includes a compressor, combustor and expander, for maintaining the operation of a terephthalic acid oxidation plant following an oxidation reactor trip comprising:
- a. retaining a concentration of oxygen in an ICOCGT combustor sufficient to sustain combustion and generate a combusted gas stream;
 - b. feeding the combusted gas stream to an ICOCGT expander, which produces a vent gas stream;
 - c. feeding the vent gas stream to a heat recovery system, with an optional auxiliary combustor, to produce recovered heat; and
 - d. using the recovered heat to maintain the operation of the terephthalic acid oxidation plant process duties.
36. The process of claim 35 further comprising: (e) feeding the recovered heat to a terephthalic acid purification stage.
37. The process of claim 35 further comprising: (e) using the recovered heat to start-up a paraxylene - air oxidation reaction.

38. The process of claim 35 further comprising: (e) feeding a portion of the recovered heat to a terephthalic acid purification stage and (f) using a portion of the recovered heat to start-up a paraxylene - air oxidation reaction.
39. The process of claim 35, wherein a portion of the recovered heat generates high grade heat as high pressure steam or hot oil.
40. The process of claim 35, wherein the pressure of the air fed to the reactor is boosted by a second compressor.
41. The process of claim 35, wherein the pressure of the gaseous stream is boosted by a second compressor prior to feeding to the ICOCGT expander.

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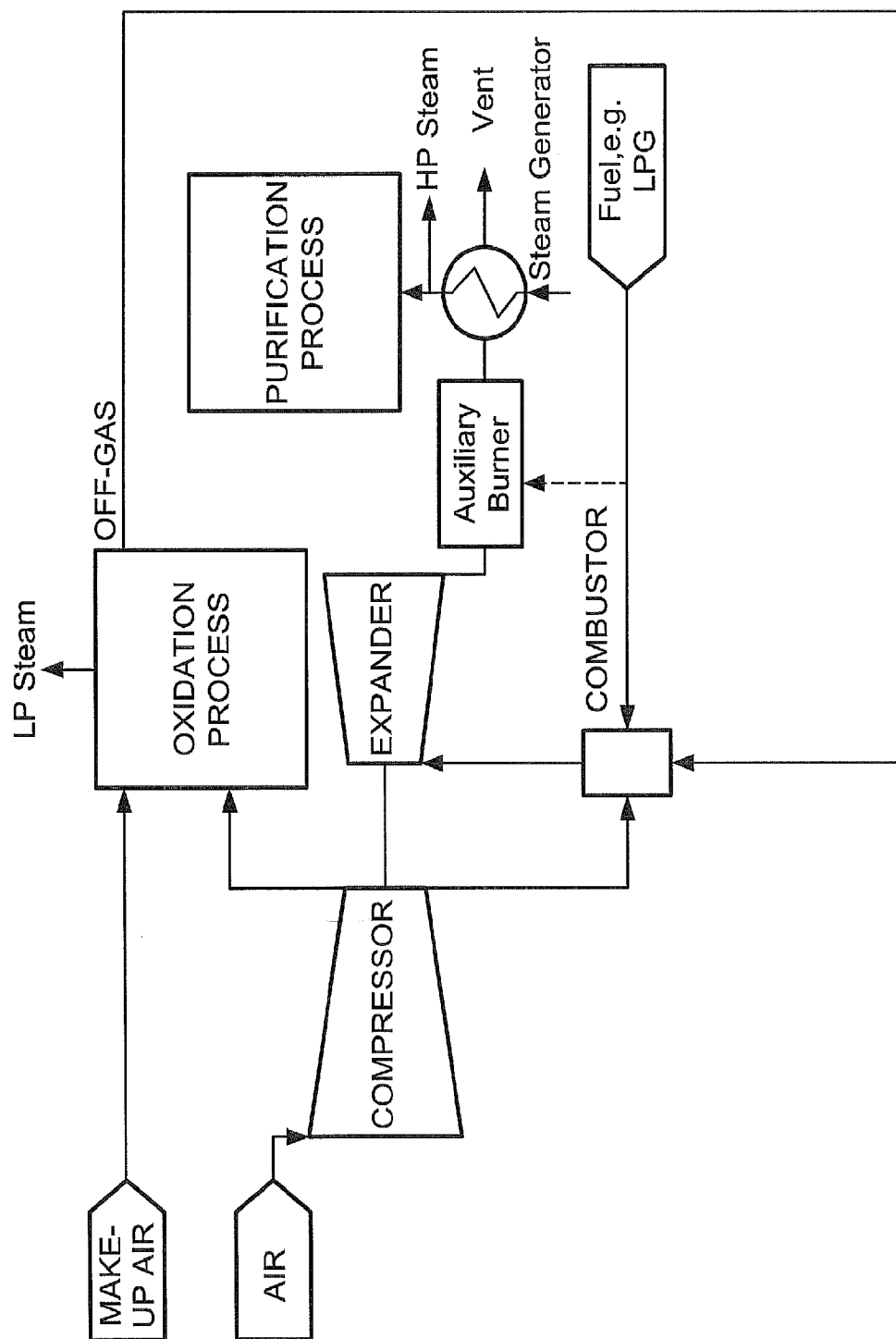


FIG. 1

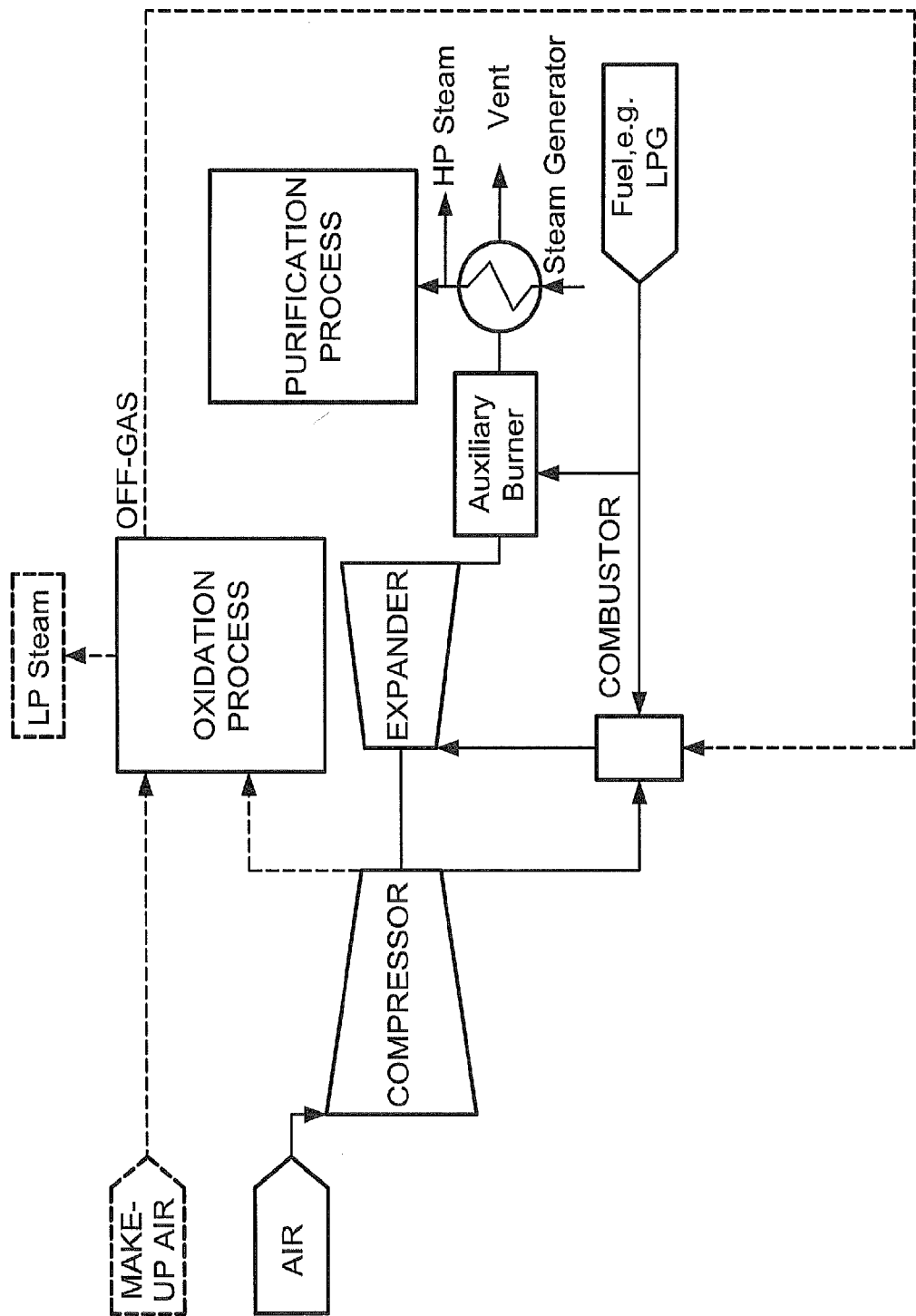


FIG. 2

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US2014/038546**A. CLASSIFICATION OF SUBJECT MATTER****F01N 3/08(2006.01)i, B01D 53/86(2006.01)i, B01D 53/75(2006.01)i, F02C 6/18(2006.01)i, F01K 25/14(2006.01)i, F23J 15/02(2006.01)i**

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)

F01N 3/08; F01K 25/14; C01B 21/38; C10G 9/36; C01B 13/02; C10B 55/00; F02C 3/20; F01K 21/04; C02F 1/72; B01D 53/86; B01D 53/75; F02C 6/18; F23J 15/02

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

Korean utility models and applications for utility models

Japanese utility models and applications for utility models

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

eKOMPASS(KIPO internal) & Keywords: ICOCGT, heat, exchanger, combustor, catalytic

C. DOCUMENTS CONSIDERED TO BE RELEVANT

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A		13–16, 28–41
Y	US 7,622,033 B1 (MCGEHEE, JAMES F.) 24 November 2009 See column 6, lines 13–48; and figures 1–2.	1–12, 17–27
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☐ Further documents are listed in the continuation of Box C.☒ See patent family annex.

* Special categories of cited documents:

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"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

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"&" document member of the same patent family

Date of the actual completion of the international search

13 October 2014 (13.10.2014)

Date of mailing of the international search report

13 October 2014 (13.10.2014)

Name and mailing address of the ISA/KR

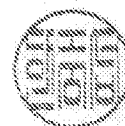
International Application Division
Korean Intellectual Property Office
189 Cheongsa-ro, Seo-gu, Daejeon Metropolitan City, 302-701,
Republic of Korea

Facsimile No. +82-42-472-7140

Authorized officer

HAN, Joong Sub

Telephone No. +82-42-481-5606



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Information on patent family members

International application No.

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