

SUPERINTENDENCIA DE INDUSTRIA Y COMERCIO	
RAD: 14-60689- -5	FECHA: 2016-04-05 08:22:49
DEP: 2020 DIRECCION DE NUEVAS CREACIONES	EVE: 378 FASE NACIONAL INCLUIDO CAPITULO I
TRA: 11 PCT-PATENTE DE INVENCION CAPITULOS I Y II	FOLIOS: 7
ACT: 519 TRASLADOINFORME	

DIRECCIÓN DE NUEVAS CREACIONES

2020
Bogotá, D.C.,

Abogado(a)/Señor(a)
LUZ CLEMENCIA DE PÁEZ

Asunto: Radicación: 14-60689- -5
Trámite: 11
Evento: 378
Actuación: 519
Oficio: 3649
Folios: 7

Patente de Invención	X			Patente de Modelo de Utilidad	
Vía Nacional					
Vía PCT (Fase Nacional)	X	Capítulo I	X	Capítulo II	
No. Solicitud Internacional	PCT/US2012/051684				
Fecha de Presentación Internacional	21/08/2012				

Como resultado del examen de fondo realizado, con fundamento en el Artículo 45 de la Decisión 486 de la Comisión de la Comunidad Andina, se comunica:

1. Documentos estudiados

Descripción:	Rad. N° 14-060689-00000-0000	20/Marzo/2014
Reivindicaciones:	Rad. N° 14-060689-00004-0000	18/Enero/2016
Dibujos:	Rad. N° 14-060689-00000-0000	20/Marzo/2014
Prioridad:	US 61/525,899	22/Agosto/2011
	US 13/590,424	21/Agosto/2012

2. Análisis de la Prioridad

Se acepta la reivindicación de prioridad porque ésta solicitud fue presentada dentro del plazo establecido (Art. 9 D 486) y su contenido técnico corresponde con el de la prioridad reivindicada.

3. Objeto de la invención

De acuerdo con lo establecido en el numeral 1.2.2.2 del Capítulo Primero del Título X de la Circular Única para efectos del examen de patentabilidad, se tendrá en cuenta la tasa pagada por el solicitante al momento de comenzar el examen para las reivindicaciones adicionales; esto es que cuando la solicitud contenga más de diez (10)

reivindicaciones y no se haya pagado la tasa complementaria, sólo se estudiarán las cubiertas por la tasa pagada. Por lo tanto, se estudiarán las reivindicaciones 1 a 6 del capítulo reivindicatorio (Radicado N°. 14-060689-00004-0000).

Título de la solicitud: “Producción mejorada de ácido nítrico” (Ver página 1 del Radicado N° 14-060689-00000-0000).

El problema planteado en esta solicitud consiste en la necesidad de mejorar métodos útiles para la producción de ácido nítrico de manera que se integre la oxidación basada en ozono dentro del sistema de absorción de ácido nítrico para reducir las emisiones de óxidos de nitrógeno sin hacer cambios significativos en el proceso o modificaciones en el equipo y maximizar la producción de ácido nítrico con o sin enriquecimiento con oxígeno.

Para resolver este problema técnico, la solicitud en estudio proporciona un método para eliminar óxidos de nitrógeno desde una corriente de gas de cola de un proceso de producción de ácido nítrico que comprende agregar ozono a dicha columna de absorción en donde la columna de absorción es de múltiples etapas y el ozono se introduce en una etapa final de dicha columna de absorción y los óxidos de nitrógeno son oxidados a la forma N_2O_5 .

El objeto de la presente solicitud se relaciona con la Clasificación Internacional de Patentes (CIP): B01D 53/56.

4. De la solicitud de patente

Reivindicaciones (Art 30 D 486, Art 22 PCT)

Durante la evaluación de claridad y concisión de las reivindicaciones, esta Oficina encontró que:

- La reivindicación 1, tiene por objeto un método, sin embargo no muestran la secuencia de etapas técnicas por medio de las cuales se transforme una materia en un producto o se obtenga un resultado. Es así como los “pasos” se limitan a suministrar una serie de elementos (materias primas, equipos, etc.) pero no enseña las etapas técnicas con sus condiciones técnicas (temperaturas, flujos, presiones, etc.), por todo lo anterior esta reivindicación no es clara. Se sugiere realizar las aclaraciones respectivas o definir la invención por sus características esenciales y estructurales, teniendo en cuenta de no modificar o ampliar la material ya divulgada.
- La reivindicación 1, no es clara porque presenta efectos como: “*los óxidos de nitrógeno son oxidados a la forma N_2O_5* ”; lo cual no es permitido. Las reivindicaciones deben caracterizar el proceso por una secuencia de etapas técnicas con sus condiciones (materias primas, equipos, temperaturas, flujos, presiones, etc.), por medio de las cuales se transforme una materia en un producto o se obtenga un resultado. No se aceptan reivindicaciones que caractericen resultados, usos, ventajas o efectos.
- La reivindicación 1, no es clara porque presenta términos generales “*columna de absorción*”, el cual, aunque corresponden a un término conocido, abarca una extensa gama de posibilidades, de tal manera que sugiere de forma imprecisa que la protección se extiende a otras posibles variaciones o modificaciones. Se sugiere sustituirlas por un término preciso o un rango concreto.
- La reivindicación 3 referida a un método se incluyen características funcionales “*dicho ozono hace contacto con dichos óxidos de nitrógeno entre*

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2do Art 45

dichas placas”, no se tendrán en cuenta para el estudio ya que dichas características si bien se pueden incluir para brindar claridad al objeto a proteger, no le pueden dar novedad ni nivel inventivo a la invención. Las reivindicaciones deben caracterizar el método por una secuencia de etapas técnicas con sus condiciones técnicas para llévalo a cabo.

5. Determinación del Estado de la Técnica

El estado de la técnica se determinó con base en la fecha de presentación de la solicitud de prioridad, es decir, 22 de agosto de 2011.

Consultadas las fuentes de información con que se cuenta, se encontraron los siguientes documentos que anticipan el objeto de esta solicitud:

Ítem	Documento	Título	Fecha de Publicación
D4	Artículo 1	“Simulation and Optimization of NOx absorption system in nitric acid manufacture”	Junio/1994
D5	US 6’197.268	“Reduction of toxic substances in waste gas emissions”	6/Marzo/2001

El documento D4¹ divulga la simulación y optimización para la absorción de NO en la fabricación de ácido nítrico (introducción).

El documento D5² divulga la eliminación de óxidos de nitrógeno de una corriente de gas residual poniendo en contacto la corriente de gas residual con amoníaco, lo que reduce los óxidos de nitrógeno en nitrógeno. Óxidos de nitrógeno residual y amoniaco sin reaccionar en la corriente de gas residual que salen de los óxidos de nitrógeno etapa de reducción se oxidan a pentóxido de nitrógeno o ácido nítrico poniéndose en contacto con esta corriente de gas con ozono (Resumen).

6. Examen de Patentabilidad (Art 14 D486)

El siguiente examen de patentabilidad se realizó teniendo en cuenta las objeciones señaladas en el numeral 4 de la presente comunicación.

Nivel inventivo (Art18 D486)

La reivindicación 1 consiste en “*Un método para eliminar óxidos de nitrógeno desde una corriente de gas de cola de un proceso de producción de ácido nítrico en donde el ácido nítrico se recupera de una columna de absorción (...)*” (Ver página 30 del radicado N° 14-060689-00004-0000).

Comparación de las características técnicas esenciales, con las del estado de la técnica:

Características esenciales	D4	D5
Un método para eliminar óxidos de nitrógeno desde una corriente de gas de cola de un proceso de producción de ácido nítrico en donde:	Sistema y proceso de absorción de NOx para la fabricación de ácido nítrico (Fig. 1a, Pág. 949, primer párrafo) en una columna de platos (Pág. 948, Col. 2, último párrafo, Pág. 955, Conclusiones).	Un proceso para la eliminación de al menos un óxido de nitrógeno de una corriente gaseosa que comprende las etapas (Reivindicación 1).
El ácido nítrico se recupera	Columna de absorción para la	

1 Anexo 1: NJ Suchak y JB Joshi. Simulation and Optimization of NOx absorption system in nitric acid manufacture. AIChE journal. Junio de 1994. Págs. 944 a 956.

2[http://worldwide.espacenet.com/publicationDetails/originalDocument?](http://worldwide.espacenet.com/publicationDetails/originalDocument?CC=US&NR=6197268B1&KC=B1&FT=D&ND=&date=20010306&DB=&&locale=en_EP)

[CC=US&NR=6197268B1&KC=B1&FT=D&ND=&date=20010306&DB=&&locale=en_EP](http://worldwide.espacenet.com/publicationDetails/originalDocument?CC=US&NR=6197268B1&KC=B1&FT=D&ND=&date=20010306&DB=&&locale=en_EP)

de una columna de absorción en donde la columna de absorción es de múltiples etapas que comprende agregar ozono a dicha columna de absorción.	fabricación de ácido nítrico en el que gas NOx se absorbe en agua (primer párrafo de la Introducción) (...) se necesita operación de múltiples etapas para obtener la concentración deseada de ácido nítrico (ítem 3, Pág. 945).	No se enseña.
Y el ozono se introduce en una etapa final de dicha columna de absorción.	No se enseña.	Poner en contacto dicho gas de escape con ozono, convirtiendo de este modo al menos parte de dicho óxido de nitrógeno residual en ácido nítrico, los precursores de ácido nítrico o mezclas de los mismos (Reivindicación 1).
Y los óxidos de nitrógeno son oxidados a la forma N ₂ O ₅ .	No se enseña.	La etapa de oxidación del NOx, se lleva a cabo usando ozono como agente oxidante. Durante el curso de este paso el contenido de NO _x residual en el efluente se oxida a un estado de oxidación más alto, por lo general a N ₂ O ₅ . El N ₂ O ₅ puede ser eliminado del sistema tal como el ácido nítrico diluido (Col. 4, Líneas 26 a 32).

El documento D4 se considera el estado de la técnica cercano a la invención definida en las reivindicaciones 1 porque divulga un método para la eliminación de óxidos de nitrógeno (NOx) con la simulación y optimización para la absorción de NO en la fabricación de ácido nítrico.

La diferencia entre la invención definida en la(s) reivindicación(es) 1 y el método de D4 consiste en que este último no menciona que el ozono se introduce en una etapa final de dicha columna de absorción y que los óxidos de nitrógeno son oxidados a la forma N₂O₅.

No se evidencia un efecto técnico inesperado o sorprendente el hecho de incluir ozono en la etapa final de la columna de absorción, por cuanto el documento D4 divulga un proceso de absorción de NOx para la fabricación de ácido nítrico (Fig. 1a, Pág. 949, Párr. 1), donde la absorción de NO es un paso importante en la fabricación de ácido nítrico (...) El óxido nítrico se somete a oxidación irreversible con oxígeno en la fase gas (Pág. 945, Col. 2, sección Reacciones fase gaseosa y equilibrio), la oxidación da como resultado ácido nítrico producto que depende del exceso de oxígeno (Pág. 946, Col. 2, Parr.1; Pág. 955, Conclusiones, punto 2), que con relación al método propuesto, soluciona el mismo problema técnico, que consiste en la reducción de las emisiones de óxidos de nitrógeno con la formación de ácido nítrico con o sin enriquecimiento con oxígeno, por lo cual, el efecto sería el mismo.

Por lo tanto, el problema técnico objetivo que pretende resolver esta invención se puede formular así: ¿cómo obtener un método para eliminar óxidos de nitrógeno de forma alternativa a la revelada en D4?

Sin embargo, la utilización de ozono para oxidar los óxidos de nitrógeno con la obtención de ácido nítrico, como alternativa para eliminar óxidos de nitrógeno de una corriente de gas y obtener ácido nítrico ya está divulgada en el documento D5 que se refiere a un proceso para la eliminación de al menos un óxido de nitrógeno de una corriente gaseosa que comprende (...) poner en contacto dicho gas de escape con ozono, convirtiendo de este modo al menos parte de dicho óxido de nitrógeno residual en ácido nítrico, precursores de ácido nítrico o mezclas de los mismos (Reivindicación 1, resumen), donde, la etapa de oxidación del NOx, se lleva a cabo usando ozono como

agente oxidante. Durante el curso de este paso el contenido de NOx residual en el efluente se oxida a un estado de oxidación más alto, por lo general a N₂O₅. El N₂O₅ puede ser eliminado del sistema tal como ácido nítrico diluido (Col. 4, Líneas 26 a 32).

En consecuencia, la persona del oficio normalmente versada en la materia, incluiría ozono en la columna de absorción para oxidar los óxidos de nitrógeno a la forma N₂O₅ y obtener ácido nítrico de D5 en el método de D4 para llegar así al objeto de la reivindicación 1 de la solicitud. Por lo cual se considera obvia. Cabe decir que los documentos D4 y D5 no enseñan que el ozono se introduzca en la etapa final de la columna de absorción, sin embargo, el documento D4 enseña que se necesita la operación de varias etapas para conseguir la concentración deseada de HNO₃. Cada etapa consta de una sección de absorción y una sección de oxidación. Por ejemplo, en el caso de una columna de platos perforados, la absorción se produce en la placa y la oxidación se produce en el espacio vacío entre las dos placas. La distancia de la base depende de la extensión deseada para la oxidación. El grado de absorción en una placa es también una variable (Pág. 945, Col. 1, punto 3), por lo cual, dado que la invención no muestra un efecto técnico sorprendente en relación al estado de la técnica, una persona versada en la materia enfrentada al problema técnico de oxidar los óxidos a la forma N₂O₅, estaría motivada a introducir el ozono en la etapa final para disponer de mayor tiempo de residencia y asegurar la formación de N₂O₅ para la formación de ácido nítrico, por lo cual se considera obvia. Vale la pena decir, que la solución al anterior problema técnico objetivo se encuentra dentro de un diseño y optimización de procesos³, lo cual se encuentra dentro de la práctica habitual de la persona versada en la materia que trabaje en el diseño de procesos de separación.

Ahora bien, el documento D1 divulga las características de las reivindicaciones dependientes así:

- Reivindicación 2: En el proceso comercial de fabricación de ácido nítrico, una gran Número (superior a 50) de las etapas de adsorción y oxidación se han usado (Pág. 944, Col. 2, Párr. 6).
- Reivindicación 3: Cada etapa consta de una absorción sección y una sección de oxidación. Por ejemplo, en el caso de una columna de platos perforados, la absorción se produce en la placa y la oxidación no se produce en el espacio vacío entre las dos placas. La distancia de la base depende de la extensión de la deseada oxidación. (...) (Pág. 945, Col. 1, punto 3).
- Reivindicaciones 4 y 5: La concentración de ácido nítrico producto depende del (...) exceso de oxígeno (Pág. 955, Conclusiones, punto 2).
- Reivindicación 5: El efecto de la presión en el volumen de oxidación se muestra en la Figura 4 (...) El volumen aumenta con una disminución de la presión (Pág. 951, punto 3), por lo cual, la persona versada en la materia estaría motivada a incluir el ozono a la presión de dicha columna de absorción.

Puesto que las reivindicaciones dependientes 2 a 6 no mencionan características inventivas adicionales tampoco se pueden considerar inventivas.

7. Conclusión

Los requisitos de Patentabilidad de la presente solicitud están afectados así:

Ítem	Documento	Reivindicaciones afectadas	Requisito que afecta
D4	Artículo 1	1 a 6	Nivel Inventivo
D5	US 6'197.268	1	Nivel inventivo

³ Perry, Manual del Ingeniero Químico. Tomo I. Sección 2. Sexta edición. 1992. Págs. 2-81 a 2-85.
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8. Respuesta a los argumentos del señor solicitante

Argumentos con respecto al estudio de novedad y nivel inventivo

1. El señor solicitante reitera que “... D1 no enseña ni sugiere la alimentación de ozono en la última etapa de la columna de absorción de multietapas (...) Mientras que el ozono es utilizado en D1, este se utiliza en un primer paso como agente oxidante para oxidar los óxidos de nitrógeno (...) en todas las etapas, la reacción del ozono con los óxidos de nitrógeno forman N_2O_5 en lugar de NO_2 y N_2O_3 (...) D2 no enseña ni sugiere todos y cada uno de los elementos contenidos en la reivindicación 1 de la presente invención (...) De igual manera, tampoco hay enseñanzas de que la columna de absorción es una columna de absorción de múltiples etapas ni que el agente de tratamiento químico, ozono, se introduce en la etapa final de la columna de absorción. D2 tampoco enseña ni discute que los óxidos de nitrógeno en la corriente del gas efluente son oxidados a la forma N_2O_5 ”.

Se aclara que tiene razón porque a la luz de la nueva reivindicación 1, los D1 y D2 no enseñan una columna de absorción de múltiples etapas ni que los óxidos de nitrógeno son oxidados a la forma N_2O_5 , por lo cual, se trasladan los documentos D4 y D5 que afectan por nivel inventivo la solicitud.

Cabe decir, que el método reclamado se caracteriza de forma muy general, puesto que no se indica claramente las etapas con las condiciones técnicas para obtener un producto y/o un resultado, además, incluyen se incluyen resultados y/o efectos tal como: “los óxidos son oxidados a la forma N_2O_5 ”, lo cual no es permitido, puesto que la citada reivindicación incluiría no sólo la solución propuesta por el solicitante, sino todas las alternativas presentes o futuras que lleguen a ese resultado, por lo cual, no le puede dar altura inventiva a la invención. Se reitera que un método se caracteriza por sus etapas con las condiciones técnicas para llevarlo a cabo.

En cumplimiento del artículo 45 de la Decisión 486 de la Comisión de la Comunidad Andina, se le indica que debe dar respuesta dentro del término de sesenta (60) días contados a partir de la fecha de notificación de la presente comunicación. En caso de no dar respuesta al presente requerimiento, o si a pesar de la respuesta subsistieran los impedimentos para la concesión, se denegará la patente.

Si como respuesta a este requerimiento el solicitante llegara a modificar: i) el capítulo reivindicatorio, ii) la descripción de la invención a proteger, iii) o presente un nuevo capítulo reivindicatorio, y desee que se realice un nuevo examen de patentabilidad a esta modificación, no deberá pagar la tasa de modificación voluntaria pero sí la correspondiente a la tasa de examen de patentabilidad. En todo caso, el número de requerimientos por no patentabilidad estará supeditado a que el término del estudio de patentabilidad no sea superior a 18 meses, contados desde la publicación de la solicitud de patente de invención. Adicionalmente, se le recuerda al solicitante que si como respuesta a este requerimiento llegara a modificar el capítulo reivindicatorio y éste contenga más de diez (10) reivindicaciones deberá pagar la tasa por reivindicación adicional.

Notifíquese el presente oficio conforme a lo dispuesto en el numeral 5.2, literal e), del capítulo quinto del título primero de la Circular Única No. 10 de 2001.



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El anterior requerimiento fue notificado por fijación en lista, de fecha 2016-04-12

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Simulation and Optimization of NO_x Absorption System in Nitric Acid Manufacture

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A mathematical model has been developed for the prediction of the optimum design of packed and plate columns for the manufacture of nitric acid. The effects of inlet NO_x composition, extent of oxidation and extent of absorption in each stage, temperature, and pressure have been included in the model. The optimization of the preoxidizer and the condenser has also been discussed.

Introduction

Absorption of NO_x is an important step in the manufacture of nitric acid. Absorption of NO_x gas is probably the most complex when compared with other absorption operations. This is for several reasons. First, the NO_x gas is a mixture of several components consisting of NO, NO₂, N₂O₃, N₂O₄, and so on. The absorption of NO_x gas in water results into two oxyacids, nitric acid, and nitrous acid. Secondly, several reversible and irreversible reactions occur in both gas and liquid phases. Thirdly, simultaneous absorption of many gases occurs followed by chemical reaction. Also, simultaneous desorption of many gases occurs preceded by chemical reaction. For example, the absorption of NO₂, N₂O₃, and N₂O₄ is accompanied by chemical reaction whereas the desorption of NO, NO₂, and HNO₂ is preceded by chemical reaction. Finally, heterogeneous equilibria prevail between gas-phase and liquid-phase components. Sherwood et al. (1975) and Joshi et al. (1985) have reviewed these aspects of NO_x absorption.

For the process design of NO_x absorption towers, it is necessary to understand the combined effects of several equilibria, including the rates of mass-transfer and chemical reaction. Further, substantial heat effects are associated with NO_x absorption; therefore, temperature variations need to be taken into account in the process design. There have been outstanding attempts in this direction. For instance, Koval and Peters (1960), Andrew and Hanson (1961), Koukolik and Marek (1968), Carleton and Valentin (1968), Hoftizer and Kwanten (1972), Makhotkin and Shamsutdinov (1976), Holma and Sohlo (1979), Emig et al. (1979), Counce and Perona (1979, 1980, 1983), Joshi et al. (1985), Miller (1987), and Wiegand et al. (1990) have reported various aspects of the process design of packed

columns, plate columns, and packed bubble columns used for the manufacture of nitric acid. These attempts will be strengthened if the following important features are included in the process design.

(1) The rates of absorption of NO₂, N₂O₃, and N₂O₄ in nitric acid are different from those in water. The rates decrease with an increase in the concentration of nitric acid.

(2) It is known that for a given set of partial pressures of NO, NO₂, and N₂O₄, there exists a certain limiting concentration of nitric acid beyond which no absorption of N₂O₄ and NO₂ occurs (Carberry, 1958). This heterogeneous equilibrium substantially reduces (even three to four times) the rates of absorption of NO₂, N₂O₃, and N₂O₄, and the extent of reduction increases as the nitric acid concentration approaches the equilibrium value.

(3) A substantial quantity of nitric acid is formed in the gas phase, particularly at high temperatures and high partial pressure of NO_x. Therefore, HNO₃ formation needs to be included in the mathematical model.

(4) A detailed energy balance also needs to be incorporated in the model.

Table 1 summarizes the earlier work. Though the mathematical model of Suchak et al. considers all the above aspects, it was developed for a case of a four-stage absorption system. In the commercial process of nitric acid manufacture, a large number (exceeding 50) of absorption and oxidation stages are used. Under these conditions, there are several aspects which need to be considered for the reliable and optimal design. These are:

(1) For every mole of NO_x absorber, 1/3 mol is desorbed in the form of NO. Thus, the oxidation rates are linked with the absorption/desorption rates.

(2) The rate of absorption of NO₂ as such is negligible.

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Table 1. Summary of Previous Work

	Dependence of $H\sqrt{kD}$ on HNO_3 Conc.	Role of Hetero- ogeneous Equil. on Abs. Rate	Formation HNO_3 in Gas Phase	Mass Transfer of H_2O , HNO_3 and/or HNO_2 from/to Gas Phase from/to Liquid Phase	Complete Energy Balance
Emig et al. (1979)*	NC	NC	NC	NC	C
Holma & Sohlo (1979)**	NC	NC	NC	NC	C
Miller (1987)	C	NC	NC	NC	NC
Wiegand et al. (1990)*	C	NC	NC	NC	NC
Suchak et al. (1991)	C	C	C	C	C

*The mechanism of absorption with chemical reaction needs to be included in the overall rate equation.

**The plate efficiency needs to be calculated for the case of NO_x absorption.

C = Considered

NC = Not considered

However, in the presence of NO , NO_2 forms N_2O_3 and HNO_2 in the gas phase. The rate of N_2O_3 and HNO_2 absorption are very high. Thus, the presence of sufficient NO enhances the rate of absorption.

(3) The maximum permissible concentration of HNO_3 (1) decreases with an increase in mole fraction of NO . As the absorption continues, the mole fraction of NO increases because of the absorption of N_2O_4 , N_2O_3 , and HNO_3 (g). Therefore, the multistage operation is needed for getting the desired concentration of HNO_3 (1). Each stage consists of an absorption section and an oxidation section. For instance, in the case of a sieve plate column, the absorption occurs on the plate and the NO oxidation occurs in the empty space between the two plates. The plate spacing depends upon the extent of desired oxidation. The extent of absorption on a plate is also a variable.

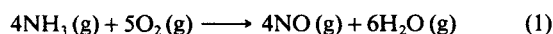
(4) The effect of temperature is multifold. The rate of NO oxidation decreases whereas the rate of absorption increases with an increase in temperature. The conversion of NO_2 to N_2O_4 is favorable at lower temperature. Further, for a given NO_x composition in the gas space, the maximum permissible HNO_3 (1) concentration increases with a decrease in temperature.

(5) Total pressure is a very strong parameter. The rate of NO oxidation is proportional to the cube of pressure and the rates of absorption also increase with an increase in total pressure.

Since all the above parameters strongly interact, detailed understanding is needed for the selection of optimum design and operating parameters.

Mathematical Model

In the commercial nitric acid plant, the mixture of ammonia with air is passed over catalyst gauze at temperature and pressure in the range of $800\text{--}850^\circ\text{C}$ and $0.3\text{--}2\text{ MPa}$, respectively. The following is a major reaction:



This is an exothermic oxidation reaction with a short residence time. Heat liberated is advantageously removed in heat recovery section to produce superheated steam, to preheat air, and in certain cases to preheat the tail gas. The gas stream leaving the heat recovery section is at a temperature above dew

point (in a typical case 200°C) and is further cooled in a cooler/condenser before feeding it to an absorber.

The condensate is a weak nitric acid solution which is added up at an appropriate location in the absorption column.

Model for the cooler/condenser

In the cooler, the gas stream is directly contacted to weak aqueous solution of nitric acid. Mainly two types of coolers are employed: (i) spray type, where an aqueous weak acid solution is sprayed in the gas stream; (ii) bubble column type where the gas is bubbled through a pool of liquid. In both types of coolers, the weak nitric acid solution is directly brought in contact with the gas stream.

Condensers employed are generally large surface area heat exchangers. The hot gas from the heat recovery stream is passed over the cooler surface where part of water vapor condenses.

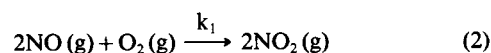
In cooler as well as condenser, during cooling, many chemical reactions and chemico-physical phenomena occur. They are: (i) oxidation of nitric oxide; (ii) formation of higher nitrogen oxides; (iii) condensation of water and oxy acids; (iv) absorption of nitrogen oxides.

In the process design of a nitric acid plant, the design of cooler/condenser is very important for obtaining the desired concentration of the product acid from the absorption section. Therefore, a mathematical model for the cooler/condenser is presented below.

Gas-phase reactions and equilibria

The gas entering the condenser consists of NO_x gases, nitrogen, oxygen, and water vapor. Nitric oxide undergoes irreversible oxidation with oxygen in the gas phase.

The oxidation reaction is expressed as:



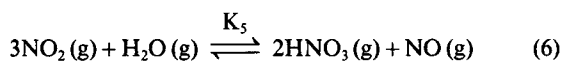
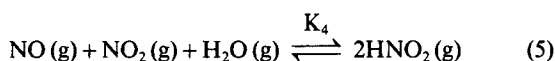
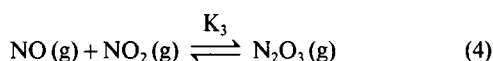
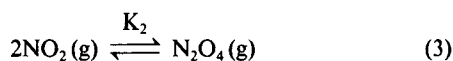
Joshi et al. (1985) have reviewed the published literature on NO oxidation. It is believed that NO oxidation proceeds by dimerization of NO is followed by oxidation by oxygen to form N_2O_4 . The oxidation reaction is second-order with respect to NO and first-order with respect to oxygen.

The gas phase consists of NO , NO_2 , N_2O_3 , and N_2O_4 . In the

Table 2a. Gas-Phase Reactions

Eqs.	Equilibrium and Rate Constants	
1	$\log_{10} k_1 = 652.1/T - 4.747$	$(\text{kN/m}^2)^{-2} \cdot \text{s}^{-1}$
2	$\log_{10} K_2 = 2,993/T - 11.232$	$(\text{kN/m}^2)^{-1}$
3	$\log_{10} K_3 = 2,072/T - 9.2397$	$(\text{kN/m}^2)^{-1}$
4	$\log_{10} K_4 = 2,051.17/T - 8.7385$	$(\text{kN/m}^2)^{-1}$
5	$\log_{10} K_5 = 2,003.8/T - 10.763$	$(\text{kN/m}^2)^{-1}$

presence of water vapor (which is generally the case) oxyacids (HNO_2 and HNO_3) are also present in the gas phase. Complex equilibria prevail in the gas phase which can be described by the following equations:



The reaction rate constant k_1 and the gas-phase equilibria constants $K_2 \dots K_5$ were reported by Joshi et al. (1985) and are presented in Table 2a.

The total number of moles in the gas per mole of inerts is obtained by adding ratios of all gaseous species to one mole of inerts:

$$Y_T = Y_{\text{NO}} + Y_{\text{NO}_2} + Y_{\text{N}_2\text{O}_4} + Y_{\text{N}_2\text{O}_3} + Y_{\text{HNO}_2} + Y_{\text{HNO}_3} + Y_{\text{H}_2\text{O}} + Y_{\text{O}_2} + 1.0 \quad (7)$$

where,

Table 2b. Heats of Reaction

Reactions	Std. Heat of Reaction (25°C) $\text{kcal} \times 10^{-3}$
<i>Reactions in Gas Phase</i>	
$2\text{NO}_{(\text{g})} + \text{O}_{2(\text{g})} \longrightarrow 2\text{NO}_{2(\text{g})}$	$\Delta H_1 = -13.64$ per kmol NO oxidized
$2\text{NO}_{2(\text{g})} \longrightarrow \text{N}_2\text{O}_{4(\text{g})}$	$\Delta H_2 = -13.69$ per kmol N_2O_4 formed
$\text{NO}_{(\text{g})} + \text{NO}_{2(\text{g})} \longrightarrow \text{N}_2\text{O}_{3(\text{g})}$	$\Delta H_3 = -9.55$ per kmol N_2O_3 formed
$3\text{NO}_{2(\text{g})} + \text{H}_2\text{O}_{(\text{g})} \longrightarrow 2\text{HNO}_{3(\text{g})} + \text{NO}_{(\text{g})}$	$\Delta H_4 = -4.23$ per kmol HNO_3 formed
$\text{NO}_{(\text{g})} + \text{NO}_{2(\text{g})} + \text{H}_2\text{O}_{(\text{g})} \longrightarrow 2\text{HNO}_{2(\text{g})}$	$\Delta H_5 = -4.905$ per kmol HNO_2 formed
<i>Reactions in the Liquid Phase</i>	
per kmol NO_2 absorbed	$\Delta H_6 = -12.82$
per kmol N_2O_4 absorbed	$\Delta H_7 = -12.04$
per kmol N_2O_3 absorbed	$\Delta H_{10} = -9.55$
per kmol HNO_2 absorbed	$\Delta H_{13} = +5.71$
per kmol HNO_3 absorbed	$\Delta H_{11} = -9.36$
per kmol HNO_2 absorbed	$\Delta H_{12} = -9.9$

$$Y_{\text{N}_2\text{O}_4} = K_2 (Y_{\text{NO}_2})^2 P_T / Y_T \quad (8)$$

$$Y_{\text{N}_2\text{O}_3} = K_3 Y_{\text{NO}} Y_{\text{NO}_2} P_T / Y_T \quad (9)$$

$$Y_{\text{HNO}_2} = [K_4 Y_{\text{NO}} Y_{\text{NO}_2} Y_{\text{H}_2\text{O}} P_T / Y_T]^{1/2} \quad (10)$$

$$Y_{\text{HNO}_3} = \left(\frac{K_5 (Y_{\text{NO}_2})^3 Y_{\text{H}_2\text{O}} P_T}{Y_{\text{NO}}} \right)^{1/2} \quad (11)$$

All the components of NO_x can be expressed in terms of:

(a) Total reactive nitrogen (Y_{N^*}), mole of reactive nitrogen per mole of inerts:

$$Y_{\text{N}^*} = Y_{\text{NO}} + Y_{\text{NO}_2} + 2(Y_{\text{N}_2\text{O}_4}) + 2(Y_{\text{N}_2\text{O}_3}) + Y_{\text{HNO}_2} + Y_{\text{HNO}_3} \quad (12)$$

(b) while extent of oxidation at any instance is expressed in the form of Y_{NO^*} , moles of divalent nitrogen per mole of inerts:

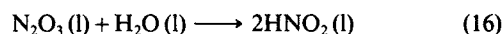
$$Y_{\text{NO}^*} = Y_{\text{NO}} + Y_{\text{N}_2\text{O}_3} + 0.5(Y_{\text{HNO}_2}) - 0.5(Y_{\text{HNO}_3}) \quad (13)$$

(c) $Y_{\text{H}_2\text{O}^*}$ is moles of water in the form of oxyacids and free water vapor per mole of inerts. It is expressed as:

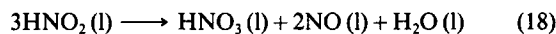
$$Y_{\text{H}_2\text{O}^*} = Y_{\text{H}_2\text{O}} + 0.5(Y_{\text{HNO}_2}) + 0.5(Y_{\text{HNO}_3}) \quad (14)$$

Condensation and liquid-phase reactions

In the cooler/condenser, due to reduction in temperature, water vapor from the gas phase condenses with simultaneous absorption of nitrogen oxides thus further altering the equilibria. Nitrogen oxides when absorbed in an aqueous acid solution form nitrous and nitric acid. The following reactions occur in the liquid phase:



HNO_2 in the bulk of liquid phase is considered to decompose to form nitric acid:



HNO_3 and H_2O are at their saturation concentrations in the gas phase. Vapor pressure of H_2O or HNO_3 over the aqueous nitric acid solution is a function of temperature and nitric acid concentration:

$$p_{\text{H}_2\text{O}} = f(T, \text{Conc}(\text{HNO}_3)) \quad (19)$$

$$p_{\text{HNO}_3} = f(T, \text{Conc}(\text{HNO}_3)) \quad (20)$$

Condensate concentration and heterogeneous equilibria

For a known composition of NO_x in the gas phase the maximum attainable concentration of nitric acid (in the liquid phase) is described by Carberry (1958):

$$K_6 = \frac{p_{\text{NO}}}{(p_{\text{N}_2\text{O}_4})^{3/2}} \quad (21)$$

Holma and Sohlo (1979) have given the following correlation for the equilibrium constant:

$$\log K_H = 30.086 - 0.0693T - (0.197 - 3.27 \times 10^{-4} T)W + 1.227 \log[(100 - W)/W^2] \quad (22a)$$

and for less than 5 percent by weight

$$\log K_H = 31.96 - 0.0693T - (3.27 \times 10^{-4} T - 0.4193)W \quad (22b)$$

where

$$K_H = K_2^{3/2} K_6 (101.33)^2 \quad (23)$$

and W is the maximum attainable HNO_3 concentration in weight percent. K_6 is given by Eq. 21.

Material balance over condenser/cooler

Here we make the following rational assumptions:

(1) All reacted nitrogen oxide entering the condenser is in the form of nitric oxide.

(2) Gases leaving the condenser are in equilibrium with condensate.

(3) Gases leaving the condenser are saturated with nitric acid and water vapor.

Water enters the condenser in the form of water vapor. Partly it condenses and partly it reacts to form nitric and nitrous acid in both liquid and gas phases. Equating the incoming and outgoing streams of condenser for H_2O^* :

$$G(Y_{\text{H}_2\text{O}}^*, i) = G(Y_{\text{H}_2\text{O}}^*, c) + L_C(1 + 0.5X_C) \quad (24)$$

As stated in the assumption, NO_x entering the condenser is in the form of nitric oxide while due to oxidation, gas-phase equilibrium, condensation, and absorption in the condenser, it is present in both gas and liquid phases. The balance for reactive nitrogen gives:

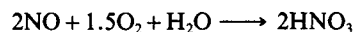
$$G(Y_{\text{N}}^*, i) = G(Y_{\text{N}}^*, c) + L_C(X_C) \quad (25)$$

Due to oxidation of nitric oxide to nitrogen dioxide, oxygen concentration in the gas phase reduces. The material balance for oxygen is given by:

$$G(Y_{\text{O}_2, i}) = G(Y_{\text{O}_2, c}) + L_C(0.75X_C) + G(Y_{\text{N}}^*, c - Y_{\text{NO}}^*, c) \quad (26)$$

The second term on righthand side needs some explanation. It has been assumed earlier that all the NO_x entering the cooler/condenser is in the form of NO . This NO is converted to HNO_3 through several stages: (a) NO oxidation to NO_2 according to Eq. 2; (b) conversion of NO and NO_2 to N_2O_3 , N_2O_4 , and HNO_2 according to Eq. 3, 4, and 5; (c) absorption of NO_2 , N_2O_3 , and HNO_2 to form HNO_3 and HNO_2 ; (d) decomposition of HNO_2 and desorption of NO . The desorbed NO need to be oxidized again. Thus, the stoichiometric oxygen requirement

is greater than that indicated by Eq. 2. All the above steps may be combined to give the following equation:



Thus, it can be seen that, for the formation of 1 mol of HNO_3 , 0.75 mol of oxygen is needed.

Method of solution

For the estimation of gas-phase composition and quantity of condensate (at specified temperature and concentration of condensate), we need to solve Eqs. 7-14 and 19-26. Using substitutions in Eqs. 7, 19, 24, 25, and 26 a system of five nonlinear algebraic equations having five unknowns namely Y_T , Y_{NO_2} , Y_{O_2} , L_C , and $Y_{\text{H}_2\text{O}}$ was formulated. Under most practical conditions these five variables possess large positive value. The Newton-Raphson method in conjunction with the Gauss-Jordan method was employed. The objective behind reducing these equations was to achieve single finite solution with minimum numerical iterations.

Model for oxidizer

The gases leaving the condenser are in equilibrium with the condensate concentration. In order to produce the product acid of desired concentration it is necessary to further oxidize the nitric oxide. This is achieved by providing additional volume between the condenser and the absorber. The extent of oxidation required depends on many factors such as the desired nitric acid concentration, temperature, and pressure. The oxidation volume is usually provided at the bottom of the absorption column. Here essentially an increase in the mole fraction of tetravalent oxides occurs. Temperature in this section is maintained in the range similar to the absorption temperature of the product acid. For modeling the oxidation section, we make following assumptions: (1) gas-phase flows in the plug flow manner; (2) the oxidizer is operating at the steady state; (3) gases follow ideal gas behavior.

Gas-phase reactions and equilibria

The gas-phase reactions and equilibria have been described in the previous section. The set of Eqs. 7-16 is a mathematical formulation for establishing composition of the gas phase. Suchak et al. (1991) have reduced these eight equations to four equations expressed in Y_{NO} , Y_T , $Y_{\text{H}_2\text{O}}$, and Y_{NO_2} .

For a known molar concentration of inerts, oxygen, total NO_x , and NO^* to N^* ratio, equilibrium partial pressures in the gas phase can be estimated.

Model for the oxidizer section

Mass balance across a differential height dh at height h from the bottom is given as:

(a) Divalent nitrogen balance:

$$\frac{dY_{\text{NO}}^*}{dh} = -\frac{S}{G} (k_1 (p_{\text{NO}})^2 p_{\text{O}_2} \epsilon_G) \quad (27)$$

(b) Oxygen balance:

$$\frac{dY_{O_2}}{dh} = -\frac{S}{2G} (k_1 (p_{NO})^2 p_{O_2} \epsilon_G) \quad (28)$$

Equations 27 and 28 are nonlinear differential equations. The overall oxygen and NO* balance (across the oxidizer) is established on solving these equations.

Heat balance

Oxidation of NO, formation of N_2O_3 , N_2O_4 , HNO_2 , and HNO_3 in the gas phase are exothermic. Because of these reactions significant heat changes occur. The values of reaction rate constant and equilibrium constants depend upon temperature. Heat liberated because of various reactions in the gas phase has been included in Table 2b.

If Q_T is the total heat change per unit time in the differential element then the temperature change under adiabatic conditions is given by:

$$T_e = (Q_T + m_i^0 C_p^0 T_i) / m_e^0 C_p^0 \quad (29)$$

where T_e and T_i are the temperature at the exit and the inlet of differential element.

(a) Contribution to the heat changes from the gas phase are due to the following steps:

- The rate of formation of N_2O_3 from NO and NO_2 in the differential element is given by:

$$(N_2O_3)_f = (N_2O_3)_e - (N_2O_3)_i \quad (30)$$

$$(N_2O_3)_f = G (Y_{N_2O_3,e} - Y_{N_2O_3,i}) \quad (31)$$

The rate of heat generation due to N_2O_3 formation is:

$$Q_1 = ((N_2O_3)_f) \Delta H_4 \quad (32)$$

- The rate of formation of N_2O_4 from NO_2 in the differential element is given by:

$$(N_2O_4)_f = (N_2O_4)_e - (N_2O_4)_i \quad (33)$$

$$(N_2O_4)_f = G (Y_{N_2O_4,e} - Y_{N_2O_4,i}) \quad (34)$$

The rate of heat generation due to N_2O_4 formation is:

$$Q_2 = ((N_2O_4)_f) \Delta H_3 \quad (35)$$

- The rate of formation of HNO_3 in the differential element is given by:

$$(HNO_3)_f = (HNO_3)_e - (HNO_3)_i \quad (36)$$

$$= G (Y_{HNO_3,e} - Y_{HNO_3,i}) \quad (37)$$

The rate of heat generation due to HNO_3 formation is:

$$Q_3 = (HNO_3)_f \Delta H_6 \quad (38)$$

- The rate of formation of HNO_2 in the differential element is given by:

$$(HNO_2)_f = (HNO_2)_e - (HNO_2)_i \quad (39)$$

$$= G (Y_{HNO_2,e} - Y_{HNO_2,i}) \quad (40)$$

The rate of heat liberated due to HNO_2 formation is:

$$Q_4 = (HNO_2)_f \Delta H_7 \quad (41)$$

- The rate of heat generation due to the oxidation of NO is estimated from the knowledge of the rate of NO oxidation. It may be noted that NO is consumed in the N_2O_3 and HNO_2 formation and liberated during HNO_3 formation.

The mass balance for NO across the differential element is given by:

$$NO_o = (NO)_i - (NO)_e - N_2O_3,f - 1/2 HNO_2,f + 1/2 HNO_3,f \quad (42)$$

$$= G (Y_{NO,i} - Y_{NO,e} - Y_{N_2O_3,e} + Y_{N_2O_3,i} - 1/2 Y_{HNO_2,e} + 1/2 Y_{HNO_2,i} + 1/2 Y_{HNO_3,e} - 1/2 Y_{HNO_3,i}) \quad (43)$$

The rate of heat generation due to NO oxidation is given by:

$$Q_5 = (NO_o) \Delta H_1 \quad (44)$$

Total heat change in the differential volume is summation of all the heat changes:

$$Q_T = Q_1 + Q_2 + Q_3 + Q_4 + Q_5 \quad (45)$$

Method of solution

Estimation of Gas-Phase Composition. Solution procedure described by Suchak et al. (1991) has been used.

Solution of Ordinary Differential Equations. The solution of Eqs. 27 and 28 is a boundary value problem. The flow rate and composition of the gas phase entering the oxidizer are known. The equations were solved simultaneously by the fourth-order Runge-Kutta method. Integration was carried out until the exit of the oxidizer.

Solution of Heat Balance Equations. From the above two steps the concentrations of all species are known at the inlet and exit of the differential height. Assuming all the heat is utilized as sensible heat, temperature of the gas at the exit of the differential height is estimated. For this purpose Eqs. 29–45 were used. The effect of step size for integration was examined and it was selected in such a way that the oxidizer volume is independent of the step size.

Model for the absorption column

The absorption column employed for the manufacturing nitric acid is a plate or a packed column. The configuration is shown in Figure 1a. The cool gas stream (NO_x) is introduced at the bottom of the column in the first empty section. NO in the gas phase irreversibly oxidizes to form NO_2 affecting the equilibrium concentrations of all the other constituents of NO_x . In the case of a packed column, the empty section is followed

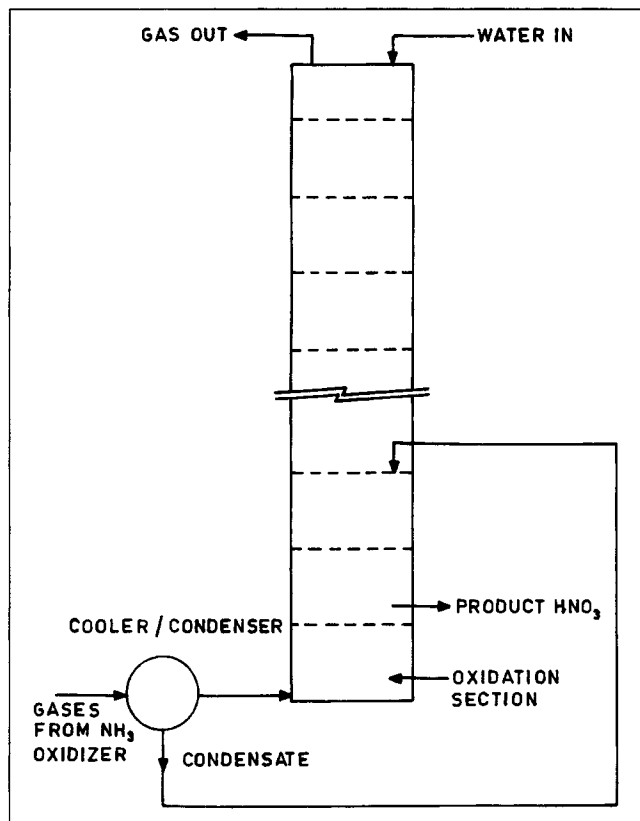


Figure 1a. NO_x absorption system for the manufacture of nitric acid.

by a packed section, which is further followed by an empty section and a packed section until desired removal of NO_x is achieved. Usually one set of empty and packed sections are housed in one column. In order to ensure complete wetting of the packings, a recirculation of loop is set up as shown in Figure 1b. A heat exchanger is provided in the external loop to remove the heat of reaction. In the case of plate columns, heat-transfer coils are placed in the pool of liquid over the plate. Two plates are separated by an empty section as shown in Figure 1c. A material balance is given by the following equations.

(1) Reacted nitrogen balance over the entire column:

$$G(Y_{N^*,i} - Y_{N^*,f}) = L_P X_P \quad (46)$$

where $Y_{N^*,f}$ is mole ratio of reacted nitrogen to inerts at the column outlet.

(2) Water and water vapor balance over the entire column:

$$G(Y_{\text{H}_2\text{O}^*,i} - Y_{\text{H}_2\text{O}^*,f}) = L_P(1 + X_P/2) - F_W \quad (47)$$

$Y_{\text{H}_2\text{O}^*,f}$ is a molar ratio of saturated water vapor to inert gas at the outlet.

(3) Oxygen balance over the entire column:

$$G(Y_{\text{O}_2,i} - Y_{\text{O}_2,f}) = 0.75L_P X_P + 0.5G(Y_{N^*,f} - Y_{\text{NO}^*,f}) \quad (48)$$

For the explanation of first term on the righthand side, kindly refer to the text below Eq. 26.

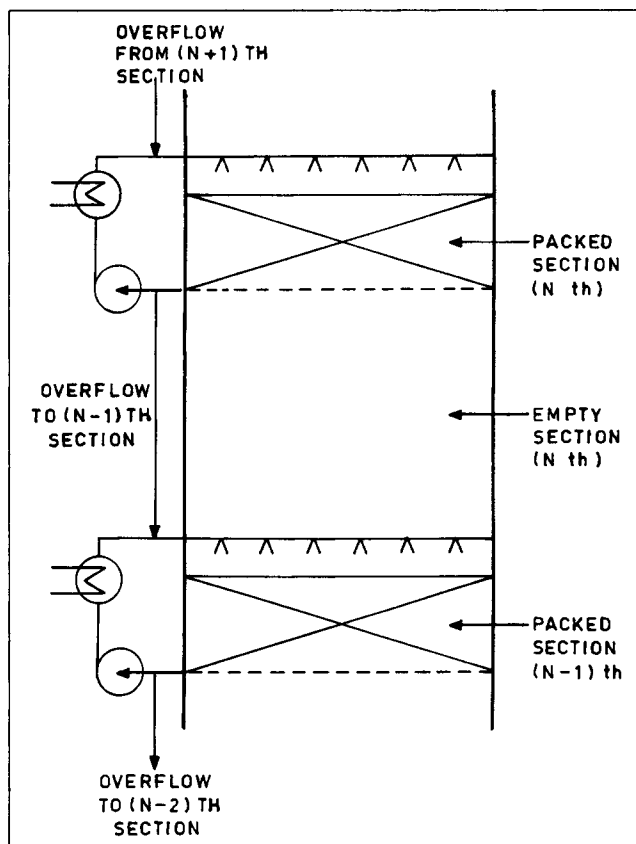


Figure 1b. One oxidation-absorption section in a packed column.

Model for empty section/space between plates

Model for empty section or the space between two consecutive plates is identical to that of an oxidizer already described in detail in the section discussing the model for oxidizer.

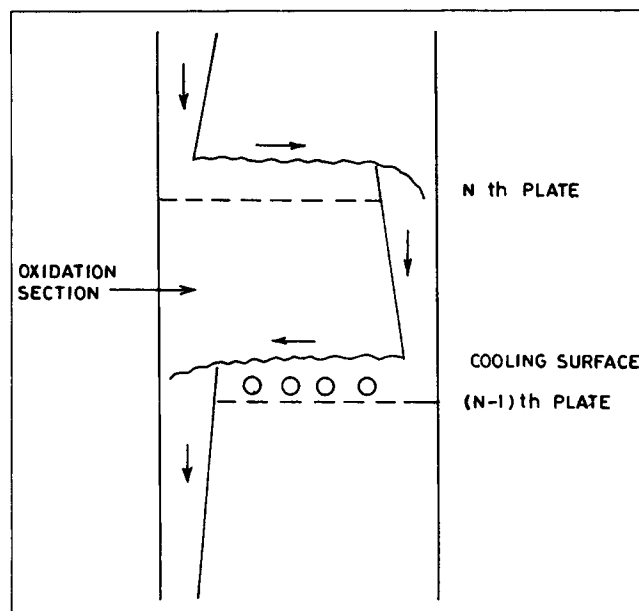


Figure 1c. One oxidation-absorption section in a plate column.

Model for absorption stage and material balance over an absorption stage

The following equations establish material balance over an absorption stage.

(1) Reacted nitrogen balance:

$$G(Y_{N^*,N-1} - Y_{N^*,N}) = L_N X_N - L_{N+1} X_{N+1} - L_S X_S \quad (49)$$

For the stage where the condensate (from cooler/condenser) is introduced $L_S = L_C$ and $X_S = X_C$, otherwise, $L_S = 0$.

(2) Water and Water vapor balance:

$$G(Y_{H_2O^*,N-1} - Y_{H_2O^*,N}) = L_N(1 + X_N/2) - L_{N+1}(1 + X_{N+1}/2) + L_S(1 + X_S/2) \quad (50)$$

Model for a packed section

A detailed model of the packed column has been presented by Suchak et al. (1991). The same model was used in the present work where the correlation for K_H values suggested by Holma and Sohlo (1979) was used. A schematic representation of one set of packed/empty sections is shown in Figure 1b.

Model for sieve plate

The liquid phase on a plate was assumed to be completely backmixed. For mass-transfer coefficients, holdup, and gas-liquid interfacial area on a sieve plate, the following correlations suggested by Zuideweg (1982) were used:

Gas side mass-transfer coefficient:

$$k_G = 0.13/\rho_G - 0.065/\rho_G^2 \quad (51)$$

Liquid side mass-transfer coefficient:

$$k_L = 2.6 \times 10^{-5}/\eta_L^{0.25} \quad (52)$$

Gas-liquid interfacial area:

$$a = 43/F^{0.3} (V_G^2 \rho_G h_i FP/\sigma)^{0.53}/H_W \quad (53)$$

$$\epsilon_L = 0.6 H_W^{0.5} \rho_H^{0.25} b^{-0.25} (FP)^{0.25}/H_W \quad (54a)$$

where:

$$FP = L'/V'(\rho_G/\rho_L)^{0.5} \quad (54b)$$

$$h_i = \epsilon_L H_W \quad (54c)$$

The absorption section model of Suchak et al. (1991) was used with design parameters of sieve plate obtained from the equations given above.

Method of solution

Computations of absorption column begins with the bottom most absorption stage. The gas-phase composition of the stream entering this absorption stage is known from the oxidizer calculations. Concentration and flow rate of product acid with-

drawn are also considered to be known. From the detailed model of an absorption stage, concentrations of water vapor and reacted nitrogen in the exit stream is obtained. Concentration and the flow rate of liquid overflow from the subsequent absorption stage are the two remaining unknowns. For this purpose Eqs. 49-50 were solved by substituting Eq. 49 in 50. These calculations were repeated for all the absorption stages until the condition ($Y_{N^*} < Y_{N^*,F}$) was satisfied. Heat balance was also established for each differential volume according to the procedure described earlier. The differential height for integration was 0.01 m for packed column and 0.002 m for plate column. There was no effect of step size below these values. Therefore, each differential volume can be considered to be isothermal. As a result, energy and species equations can be treated separately.

Results and Discussions

Simulation of a commercial plate column

Suchak et al. (1991) have shown a good agreement between model predictions and experimental observations for the case of multiple packed columns in series. It was thought desirable to simulate a sieve plate column manufacturing 750 ton/d (100% basis) of nitric acid having 58.5% concentration. This step was considered necessary before undertaking the optimization exercise. The design and operating parameters of the column are summarized in Tables 3a and 3b, respectively. The liquid submergence on each sieve plate was 50 mm. The dry pressure drop was calculated using the procedure of Fair (1984). Comparison between the predicted and the experimental concentration profiles of nitric acid are shown in Figure 2. It can be seen that the agreement is very good. The predicted outlet NO_x concentration was 1,210 ppm whereas the concentration in the commercially operating plants was 1,260 ppm. This agreement can be considered to be excellent.

Table 3a. Design Parameters of Commercial Plate Column Producing 750 tons/d Nitric Acid

Column diameter = 5.5 m
Number of plates = 73
Plate spacing = 700 mm
Liquid submergence = 50 mm
Percent free area = 3.6%
Hole diameter = 4 mm

Table 3b. Operating Parameters of Commercial Plate Column Producing 750 tons/d Nitric Acid*

- (1) Total gas flow rate before the cooler-condenser = 1.69 kmol/s
- (2) Total NO_x flow rate before the cooler-condenser = 0.1392 kmol/s
- (3) Oxygen flow rate before the cooler-condenser = 0.1356 kmol/s
- (4) Condensate temperature = 48°C
- (5) Condensate concentration = 42% (w/w)
- (6) Oxidizer volume = 49.9 m³
- (7) Oxidizer temperature = 38°C
- (8) Inlet HNO_3 concentration = 0%
- (9) Outlet HNO_3 concentration = 58% (w/w)
- (10) Total pressure at the inlet of column = 0.46 MPa

*Capacity is on the basis of 100% concentration.

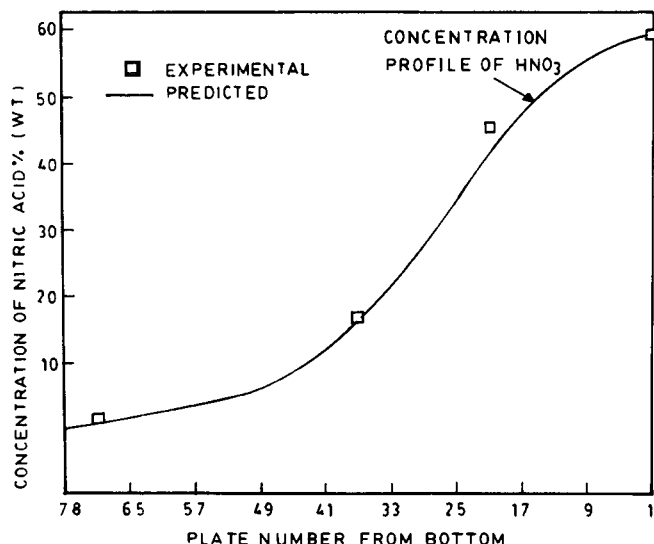


Figure 2. Simulation of a commercial nitric acid tower producing 750 ton/d.

For the design and operating parameters, refer to Table 3a.

Optimum design

(1) It has been pointed out earlier that heterogeneous equilibrium prevails between the liquid phase and the gas phase. As a result of this, for a given NO_x composition, there is a maximum permissible concentration of HNO_3 which can be produced. The concentration of HNO_3 increases with an increase in the mole fraction of tetravalent nitrogen oxides in the gas phase. Therefore, the gas phase entering the absorption column must possess sufficiently high mole fraction of tetravalent nitrogen oxides so that the absorption can occur. This condition of gas-phase composition is achieved in the oxidizer as shown in Figure 1a. Obviously, the oxidizer volume increases with an increase in the desired concentration of nitric acid.

(2) The effect of oxidation temperature on the oxidizer volume is shown in Figure 3. At any given nitric acid concentration, the oxidation volume increases with an increase in temperature. The extent of increase is very high in the temperature range of 30–45°C.

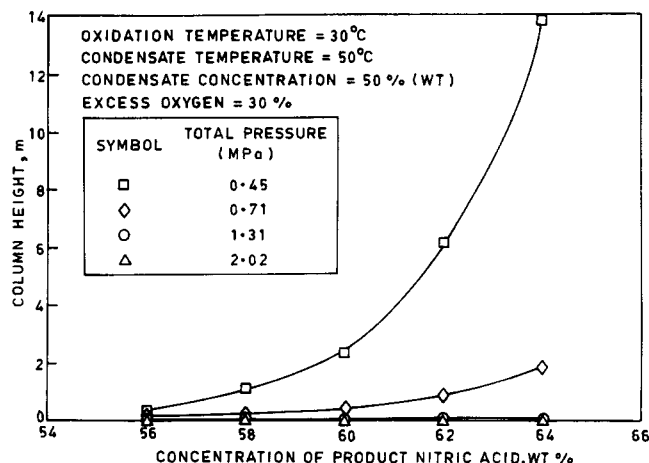


Figure 4. Effect of total pressure and product nitric acid concentration on oxidizer volume.

(3) The effect of pressure on oxidation volume is shown in Figure 4. The oxidation volume is nominal at 1.32 and 2.03 MPa. The volume increases with a decrease in pressure. The extent of increase is substantial when the pressure is reduced from 0.71 to 0.45 MPa.

(4) The effect of excess oxygen is shown in Figure 5. When the percentage excess is in the range of 10–30%, the oxidation volume decreases marginally. However, a further increase in the excess oxygen results into an increase in the oxidation volume. Such a behavior occurs because of two opposing factors. With an increase in excess oxygen, the residence time decreases due to an increase in the oxygen partial pressure. However excess oxygen is accompanied by an increase in the oxidation volume due to increase in volumetric flow rate. From Figure 5 it can be seen that 30% excess is an optimum number as far as the oxidizer volume (before the absorber) is concerned.

(5) Effects of condenser temperature and condensate concentrations are shown in Figures 6a and 6b. It can be seen from Figure 6a that the oxidation volume is negligible when the desired HNO_3 concentration is less than 60% and the condensate temperature is greater than 60°C. However, at the high temperatures of 60° and 70°C, the oxidation volume

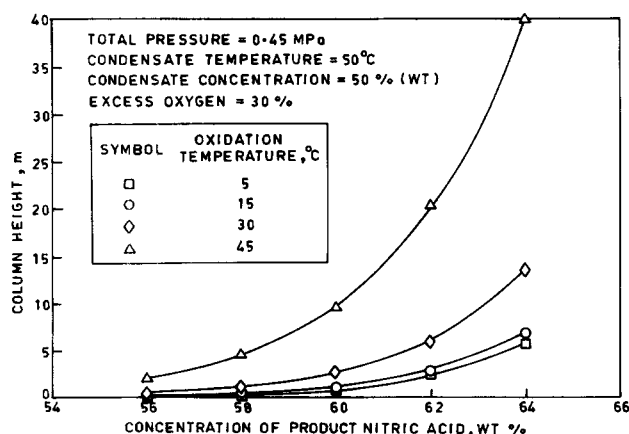


Figure 3. Effect of oxidation temperature and product nitric acid concentration on oxidizer volume.

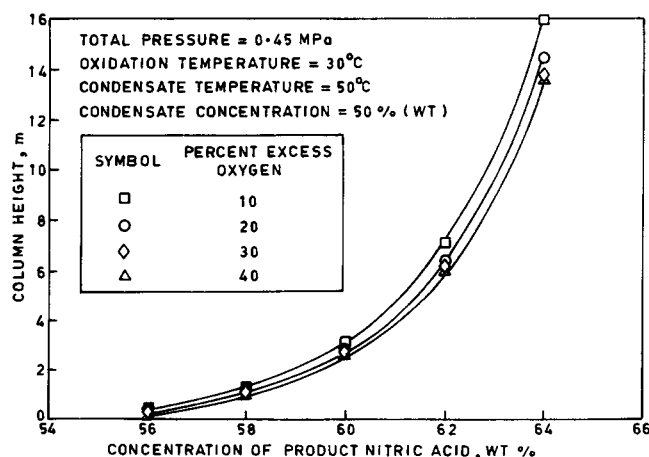


Figure 5. Effect of excess oxygen and product nitric acid concentration on oxidizer volume.

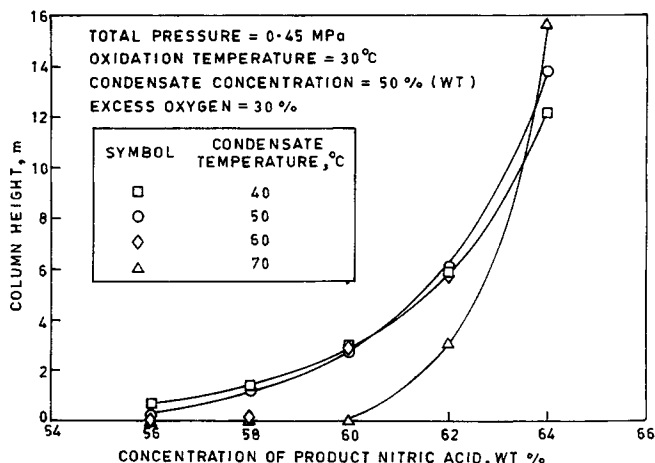


Figure 6a. Effect of condensate temperature and product nitric acid concentration on oxidizer volume.

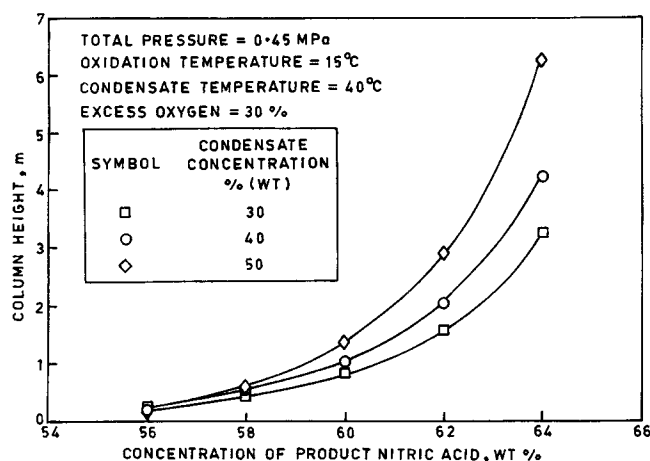


Figure 6b. Effect of condensate concentration and product nitric acid concentration on oxidizer volume.

increases sharply when the desired HNO_3 concentration increases.

When the condensate temperature is less than 50°C , the oxidation volume smoothly increases with an increase in HNO_3 concentration. It may be noted, however, that all the lines cross each other and there is a possibility of selecting an optimum oxidation volume by selecting proper condensate temperature.

From Figure 6b it can be seen that the oxidation volume increases with an increase in the condensate concentration and desired HNO_3 concentration.

In order to get an overall view regarding the number of stages needed with respect to the extent of absorption, the parameters such as pressure, temperature, and heights of packed and empty sections were varied over a wide range. The model results are given in Figures 7, 8, and 9. The capacity of absorber was 750 ton/d and 30% excess oxygen was used. Values of other parameters are listed in Table 4. From Figures 7, 8, and 9, it can be seen that the required number of stages

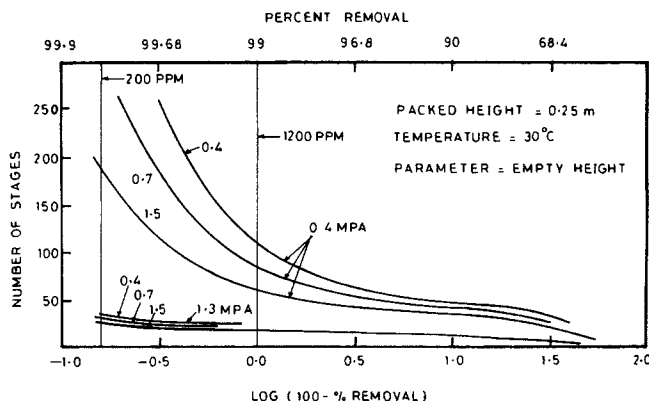


Figure 7. Effect of extent of absorption on the number of stages with pressure and height of empty section as parameters.

increases rapidly with an increase in the extent of absorption. In order to emphasize this point, the extent of conversion is shown on the top axis. Also shown are the two lines when the NO_x composition in the gas phase becomes 1,200 and 200 ppm.

The effect of total pressure and the height of empty section on the number of stages is shown in Figures 10a to 10c for packed heights of 0.25, 1.0, and 3.0 m, respectively. In all the cases, the number of stages decreases with an increase in pressure. The decrease is dramatic in the pressure range of 0.4 to 0.71 MPa. This is because the rate of oxidation varies as the cube of the pressure. However, a similar reduction is not observed when the pressure is increased from 0.71 to 1.31 MPa and further to 2.02 MPa. This is because the overall absorption becomes increasingly controlled by equilibria and the rate of oxidation is not important. This is a useful result. The oxidation volume is needed for getting sufficient tetravalent oxides so that the positive driving force prevails in the subsequent section. Such a desired composition is achieved in a small oxidation volume. In fact, at high pressures the number of stages were found to be independent of the oxidation volume (in the range covered).

From Figures 10a to 10c it can be seen that, at total pressure of 0.4 and 0.71 MPa, the number of stages decreases with an increase in the oxidation volume. Though, the number of stages

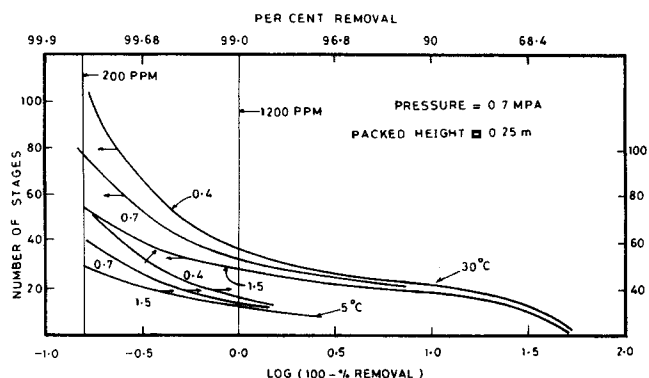


Figure 8. Effect of extent of absorption on the number of stages with temperature and height of empty space as parameter.

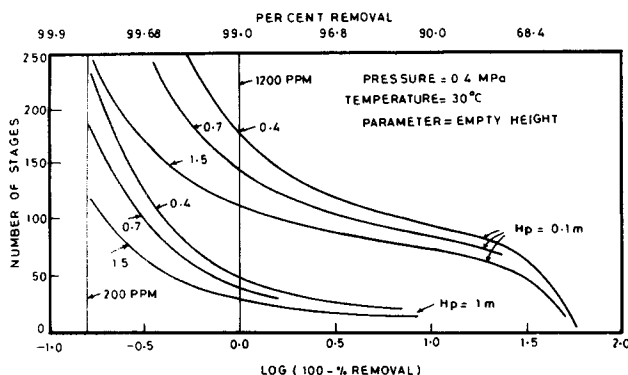


Figure 9. Effect of extent of absorption on the number of stages with the height of packed and empty sections as parameters.

decreases, it does not necessarily mean that the total height decreases. In fact, in almost all the cases, the total height was found to increase with an increase in the height of empty section (Table 5a). The increase is nominal when the empty height is increased from 0.4 to 0.7 m. This result is useful because the cost associated with a large number of stages can be reduced. However, a similar result is not obtained when the empty height is increased to 4 m and 10 m. The total height substantially increases at these empty heights. From these results it can be seen that there is an optimum level of NO oxidation per stage. A very high level of conversion needs more oxidation volume and it is not useful since some NO is liberated in the subsequent absorption section. An empty height of 0.7 m looks favorable.

The effect of packed height is shown in Figure 11 and Table 5b. It can be seen that the effect of packed height is not as dramatic as the empty height. The optimum packed height lies in the range of 0.25 to 0.5 m. The effect of temperature on the number of stages and total height is shown in Figure 12 and in Table 5c. In this case also the optimum empty height can be considered as 0.7 m and the optimum packed height is in the range of 0.25 to 0.5 m.

Though the total height is substantially low at lower temperatures, it may not be economically advantageous to operate the absorption column at low temperatures due to high refrigeration costs. However, the liquid ammonia feedstock pro-

Table 4. Values of Parameters

Values of Parameters for Figures 3 to 12

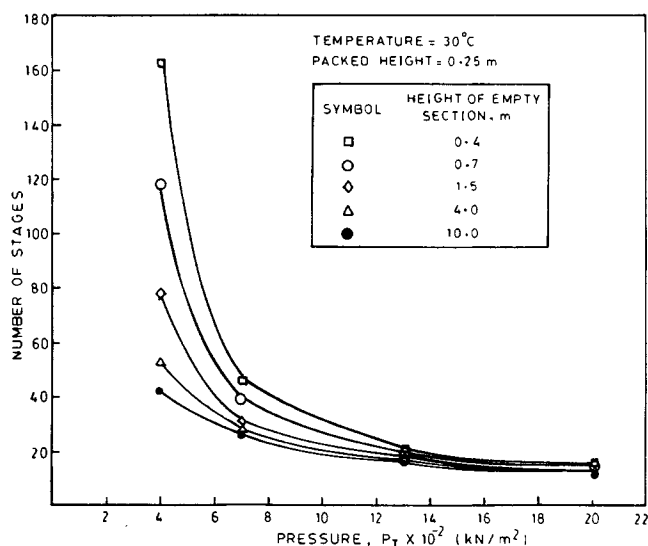
Capacity	= 750 ton/d
Total gas-flow rate before cooler condenser	= 1.69 kmol/s
Total NO _x flow rate before cooler condenser	= 0.1352 kmol/s
Oxygen flow rate before cooler condenser	= 0.1356 kmol/s
Superficial liquid velocity	= 5 mm/s
Column diameter	= 5.5 m
Packing	= Intalox saddles
Packing size	= 37 mm
Packing voidage	= 0.77

Additional Parameters for Figures 7 to 12

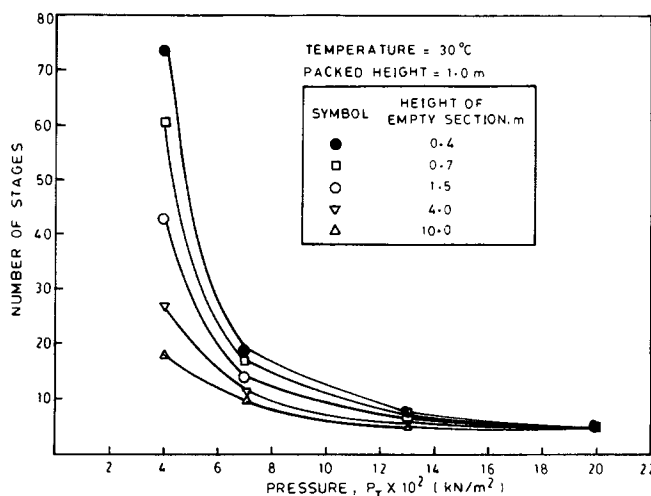
Condensate temperature	= 50°C
Condensate concentration	= 50% (wt.)
Concentration of product nitric acid	= 58% (wt.)

Additional Parameter for Figures 10 to 12

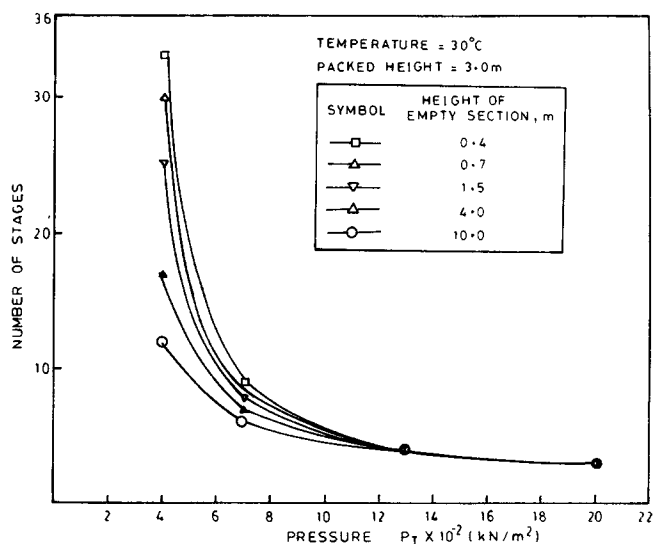
Outlet NO _x	= 700 ppm
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(a)



(b)



(c)

Figure 10. Effect of total pressure and the height of empty section on number of stages.

Packed height: A = 0.25 m; B = 1.0 m; C = 3.0 m.

Table 5a. Total Column Height*

Height of Empty Section H_E , m	Packed Height H_P , m	Total Column Height, m			
		Pressure, MPa			
		0.4	0.71	1.31	2.02
0.4	0.25	105.95	29.90	13.65	10.40
0.7	0.25	112.10	37.05	19.00	14.25
1.5	0.25	138.25	56.00	33.25	26.25
4.0	0.25	225.25	119.00	72.25	63.75
10.0	0.25	430.25	266.50	184.50	143.50
0.4	1.00	103.60	26.60	11.20	7.00
0.7	1.00	103.60	28.90	13.60	8.50
1.5	1.00	107.50	35.00	17.50	12.50
4.0	1.00	135.00	55.00	35.00	25.00
10.0	1.00	198.00	110.00	66.00	55.00
0.4	3.00	112.20	30.60	13.60	10.20
0.7	3.00	111.00	29.60	14.80	11.10
1.5	3.00	112.50	36.00	18.00	13.50
4.0	3.00	119.00	49.00	28.00	21.00
10.0	3.00	156.00	78.00	52.00	39.00

*Parameters are listed in Table 4; temperature = 30°C.

Table 5b. Total Column Height*

Height of Empty Section H_E , m	Packed Height H_P , m	Total Column Height, m			
		Pressure, MPa			
		0.4	0.71	1.31	2.02
0.7	0.10	128.00	62.40	38.40	30.40
0.7	0.25	90.25	36.10	13.65	16.15
0.7	0.50	79.20	27.60	14.40	10.80
0.7	1.00	76.20	25.50	11.90	10.20
0.7	3.00	81.40	25.90	14.80	11.10

*Parameters are listed in Table 4; temperature = 15°C.

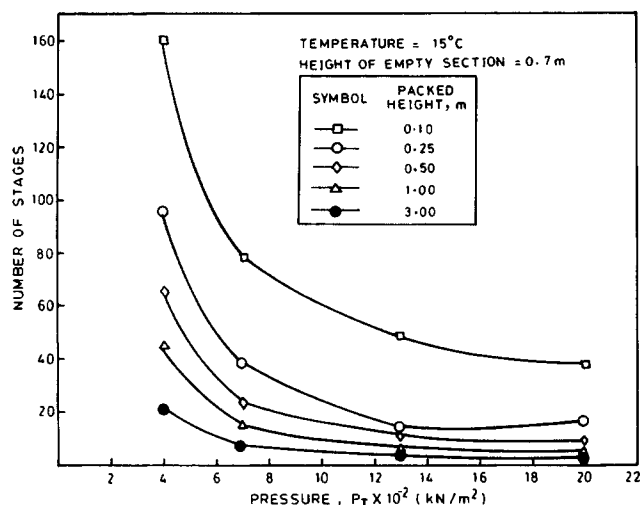
Table 5c. Total Column Height*

Height of Empty Section H_E , m	Packed Height H_P , m	Total Column Height, m			
		Temperature, °C			
		5	15	30	40
0.4	0.25	72.15	79.95	105.95	131.95
0.7	0.25	84.55	90.25	112.10	140.60
1.5	0.25	120.75	120.75	138.25	168.00
0.7	0.10	130.40	128.00	144.80	172.80
0.7	0.50	72.00	79.20	103.20	133.20
0.7	1.00	68.00	76.50	103.70	134.30

*Parameters are listed in Table 4; pressure = 0.4 MPa.

vides for some refrigeration load. The rate of heat removal due to vaporization of liquid ammonia can be used advantageously in the top section where the rate of oxidation is very low. Most of the heat is usually removed by the ambient water. Hence, the operating temperature is decided by the ambient temperature. Some refrigeration may, however, be used after establishing a clear economic advantage.

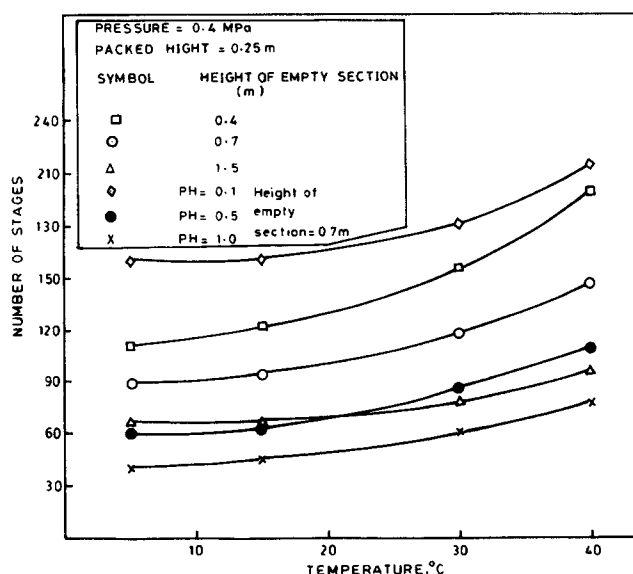
From Figures 10a to 10c and Table 5a it can be seen that the total height substantially decreases with an increase in the total pressure. The equipment cost will decrease with an in-

**Figure 11. Effect of total pressure and the packed height on number of stages.**

crease in pressure. This is because the reduction in volume and an increase in wall thickness with pressure results into an overall decrease in the metal requirement. However, this should be traded off with operating expenses for compression (after giving due credit to the energy recovery in the turbine).

From the foregoing discussion it can be seen that the optimum heights for empty section and packed section can be selected directly. However, the optimum temperature and pressure depend upon the geographical location and the cost of power.

The results on packed columns are presented in Figures 7 to 12 and Table 5 and are for the design and operating parameters listed in Table 4. For a plate column (% free area, hole diameter, and column diameter are given in Table 3a), a similar exercise resulted into the following correlations:

**Figure 12. Effect of temperature and the height of empty section and the packed height on the number of stages.**

$$0.2 < H_E < 1.5 \text{ m}$$

$$N = 482.74 H_E^{-0.434} H_W^{-0.144} \exp(-1,221.6/P_T) \times \exp(-1,563.1/T) \quad (55a)$$

$$1.5 < H_E < 10 \text{ m}$$

$$N = 28.01 H_E^{-0.177} H_W^{-0.199} \exp(658.8/P_T) \exp(-555.7/T) \quad (55b)$$

where

$$0.4 < H_E < 10 \text{ m}, \quad 0.025 < H_W < 0.1 \text{ m},$$

$$0.4 < P_T < 2.02 \text{ MPa and } 278 < T < 318 \text{ K}$$

Conclusions

(1) A mathematical model has been developed for the prediction of optimum design of packed and plate columns. The effects of inlet NO_x composition, temperature, pressure, volume of pre-oxidizer, volume of interstage oxidizers, and extent of absorption per stage have been included in the model.

(2) The concentration of product nitric acid strongly depends upon the inlet NO_x composition, temperature, pressure, and excess oxygen. For a given concentration of product nitric acid, the optimum design of preoxidizer has been presented.

(3) The extent of oxidation per stage strongly influences the number of stages. The overall equipment volume was found to increase with an increase in the extent of oxidation. However, the number of stages increases with a decrease in the extent of oxidation.

(4) The optimum design depends nominally on the extent of absorption per stage.

(5) Correlations have been developed for the number of stages for plate and packed absorption columns.

Notation

a	= interfacial area, m^2/m^3
b	= weir length per unit bubbling area, m^{-1}
C_p^O	= average specific heat of liquid phase, $\text{kcal}/\text{kmol}^\circ\text{K}$
D	= diffusivity, m^2/s
F	= fraction of hole area per unit bubbling area
FP	= flow parameter, $L'/V' \sqrt{\rho_G/\rho_L}$
F_W	= feed water, kmol/s
G	= flow rate of inerts, kmol/s
h	= height from bottom of the spray column, m
h_l	= volume of liquid per unit plate area, m^2/m^3
H	= total height of the column, m
H_e	= Henry's law coefficient, kmol/m^2 (kN/m^2)
H_E	= height of empty section, m
H_p	= height of packed section, m
H_W	= weir height, m
k	= reaction rate constant, s^{-1}
k_1	= forward reaction rate constant for Eq. 1
k_G	= gas-side mass-transfer coefficient, $\text{kmol}/[\text{m}^2 \cdot \text{s} (\text{kN}/\text{m}^2)]$
k_L	= liquid-side mass-transfer coefficient, m/s
k_n	= forward reaction rate constant for reaction n
K_6	= heterogeneous equilibrium constant defined by Eqs. 21 and 23, $(\text{kN}/\text{m}^2)^{-0.5}$
K_H	= heterogeneous equilibrium constant, Eqs. 22a and 22b, atm^{-2}
K_n	= equilibrium rate constant for reaction n
L	= molar flow rate of liquid, kmol/s

L'	= mass-flow rate of liquid, kg/s
L_p	= flow rate of water in the product acid, kmol/s
m^o	= mass-flow rate of liquid, kmol/s
N^*	= total moles of NO_x
NO^*	= total moles of divalent nitrogen oxides
p_H	= pitch of holes, m
p_n	= partial pressure of component n , kN/m^2
P_T	= total pressure of gas, kN/m^2
Q_1	= heat changes due to formation of N_2O_3 in bulk gas, kcal/s
Q_2	= heat changes due to formation of N_2O_4 in bulk gas, kcal/s
Q_3	= heat changes due to formation of HNO_3 in bulk gas, kcal/s
Q_4	= heat changes due to formation of HNO_2 in bulk gas, kcal/s
Q_5	= heat changes due to formation of NO in bulk gas, kcal/s
Q_T	= total heat changes, kcal/s
S	= cross-sectional area of the column, m^2
T	= temperature, K
V'	= mass-flow rate of gas, kg/s
V_G	= superficial gas velocity, m/s
W	= weight fraction of HNO_3 in aqueous nitric acid solution
X	= moles of nitric acid per mole of water
$Y_{\text{H}_2\text{O}}^*$	= kmol of water in form of oxyacids and free water in gas phase per kmol of inerts
Y_N^*	= kmol of reactive nitrogen per kmol of inerts
$Y_{N^*,F}$	= moles of reaction nitrogen per mole of inerts in the gas stream leaving absorber
$Y_{N^*,i}$	= moles of reacted nitrogen per mole of inerts in the gas stream from NH_3 oxidizer
Y_{NO}^*	= kmol of divalent nitrogen per kmol of inerts
$Y_{\text{NO}^*,F}$	= moles of divalent nitrogen oxides per mole of inerts in the gas stream leaving absorber
$Y_{\text{O}_2}^*$	= moles of oxygen per mole of inerts
$Y_{\text{O}_2,F}$	= moles of oxygen per mole of inerts in the gas stream leaving absorber
$Y_{\text{O}_2^*,i}$	= moles of oxygen per mole of inerts in the gas stream from NH_3 oxidizer
Y_T	= total moles of gas per mole of inerts
Y_x	= moles of gaseous component x per mole of inerts

Greek letters

ΔH_x	= heat of reaction for reaction given by Eq. x
ϵ_G	= fractional gas holdup
ϵ_L	= fractional liquid holdup
η_L	= kinematic viscosity of liquid, m^2/s
ρ	= density, kg/m^3
σ	= surface tension, N/m

Subscripts

a	= absorption
C	= condensate
e	= exit condition
f	= formation
F	= outlet
G	= gas phase
i	= inlet condition
L	= liquid phase
N	= n th stage
S	= side stream from condenser to column
T	= total

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Errata

◆ In the article titled "Memory-Integral Mass-Transfer Models for Adsorption Process Simulation" (March 1993, p. 422) by G. M. Harriott, the following corrections are made:

- On p. 425, fifth full paragraph, the last sentence should read: "Galerkin projection forces the error to be orthogonal to the basis function. . ."
- On p. 426, Table 2, the solution for Galerkin Projection: Linear Basis should contain a term of $\pi/3$, not $\pi/6$ as reported.
- On p. 428, the coefficients $\{a, b\}$ in the formulae for harmonic forcing (Eq. 28) should be multiplied by 2. The phase lag is $\phi = \tan^{-1}(b/a)$, and the asymptotic form of the amplitude A at large frequency ω is: $A \rightarrow 3/\sqrt{\omega}$.
- On p. 432, sentences 6 and 7 of the first paragraph should read: "On desorption, however, the pellet does not unload until concentration drops below $1/H$, and since the driving force for diffusion is then $O(1/H)$, a time of $O(H)$ is required to clean out the pellet. The ratio of timescales for desorption to adsorption is simply the isotherm slope at low concentration: H ."
- The title of the article by Glueckauf (1955) is "Theory of Chromatography: 10. Formulae for Diffusion Into Spheres and Their Application to Chromatography."

◆ Correct affiliations of the authors of the article titled "Two Methods of Selecting Smoothing Splines Applied to Fermentation Process Data," (April 1994, p. 716) are as follows:

Nina F. Thornhill

Dept. of Electronic and Electrical Engineering

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Search history

Search 1: TAC=(nitric acid and ozone and N2O5) (Results 19)

Title: Manufacture of nitric anhydrid

Abstract: Source: GB131334A 131,334. Gros et Bouchardy, F., (Assignees of Guye, P. A.). May 16, 1917, [Convention date]. Nitric anhydride is obtained by causing a lower oxide of nitrogen other than nitrous oxide to react with **ozone**, both agents being in the gaseous condition and in quantities exactly regulated so as to give no excess of either gas. The nitric anhydride is recovered by cooling to below -20° C., for instance to -80° C. A solvent may be employed in conjunction with the cooling, **nitric acid**, sulphuric acid, fuming sulphuric acid, and carbon tetrachloride being mentioned. The solution in sulphuric acid or fuming sulphuric acid may be used for nitrations. The gas from which the anhydride has been separated may be passed through a heat-exchanger in order to cool fresh gas.

Classifications:
International (IPC 8-9): C01B21/20 (Advanced/Invention)
International (IPC 1-7): C01B21/20 C01B21/30
CPC: C01B21/206
European: C01B21/20B
US: 423/400

Family:

Publication number	Publication date	Application number	Application date
FR496593 A	19191111		00000000
GB131334 A	00000000		00000000
US1348874 A	19200810	US19180233568	19180509

Probable Assignee: FERDINAND GROS AND BOUCHARDY

Assignee(s): (std): FERDINAND GROS AND BOUCHARDY ; FERDINAND GROS ET BOUCHARDY SO

Assignee(s): SOCIETE FERDINAND GROS ET BOUCHARDY

Inventor(s): (std): AUGUSTE GUYE LIPPE

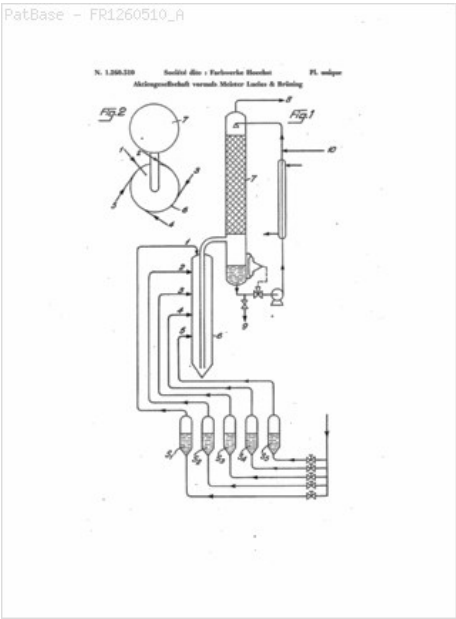
Inventor(s): GUYE LIPPE AUGUSTE

Title: Procède de preparation de formaldehyde a partir de methane

Abstract: Source: FR1260510A (Claim 1) 1. -

Machine translation: (Claim 1) 1. -

Classifications:
International (IPC 8-9): C07C45/33 (Advanced/Invention)
International (IPC 1-7): C07C47/048
CPC: C07C45/33
European: C07C45/33



Family:

Publication number	Publication date	Application number	Application date
FR1260510 A	19610505	FR19600830943	19600623

Priority:

FR19600830943 19600623

Probable Assignee: HOECHST AG

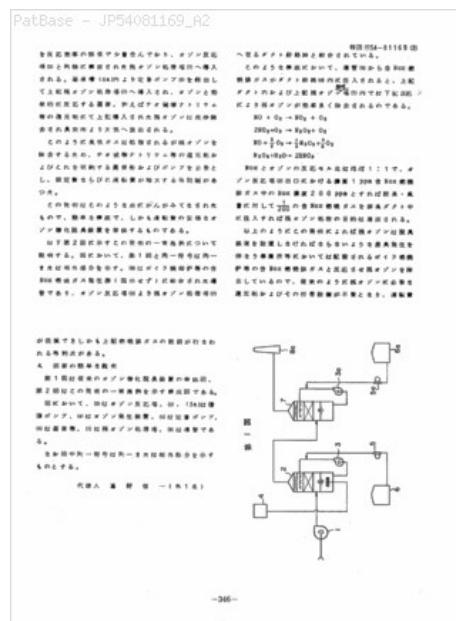
Assignee(s): (std): HOECHST AG

Assignee(s): FARBWERKE HOECHST AKTIENGESELLSCHAFT VORMALS MEIST ; FARBWERKE HOECHST AKTIENGESELLSCHAFT VORMALS MEISTER LUCIUS AND BRUENING

Abstract: Source: JP54081169A PURPOSE:An **ozone**-oxidation deodorizer capable of cutting down operation cost and also of performing the denitrification of combustion exhaust gas, having a mechanism in which a conduit pipe for combustion exhaust gas containing NOx is provided at the outlet of ozonization reactor at which unreacted **ozone** is decomposed by NOx. CONSTITUTION:In an **ozone**-oxidation deodorizer, the pipe 9 for NOx-containing exhaust gas coming out of boiler, incinerator, etc., is connected to the duct 10 leading to the residual **ozone** treatment tower 7 from the ozonization reactor 2. The residual **ozone** is decomposed by NOx in the residual **ozone** treatment tower 7 to oxidize NOx to **N2O5** which is in turn recovered as **nitric acid** by the injection of atomized water. Then, the exhaust gas deprived of NOx is discharged from the chimney 8 to the air.

International (IPC 8-9): B01D53/34 B01D53/38 B01D53/74 (Advanced/Invention);
B01D53/34 B01D53/38 B01D53/74 (Core/Invention)
International (IPC 1-7): B01D53/34

International (IPC 1-7): B01D53/34



Publication number	Publication date	Application number	Application date
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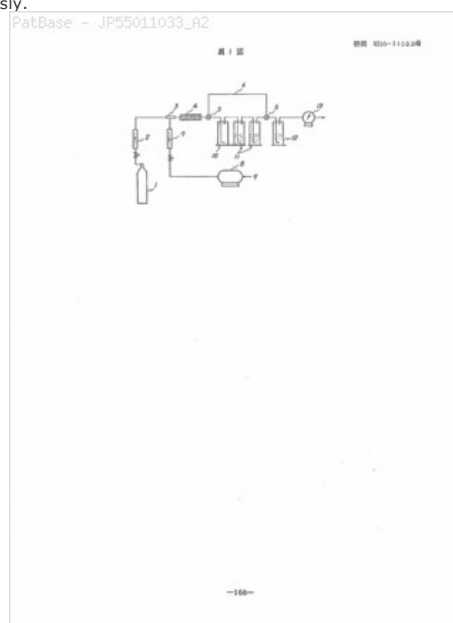
JP19770149591 19771213

Assignee(s): (std): MITSUBISHI ELECTRIC CORP

Inventor(s): (std): HAYASHI EIKICHI ; MATSUNAGA MASAYUKI

Abstract: Source: JP55011033A PURPOSE:To sample nitrogen oxides and sulfur oxides simultaneously in an easy and correct manner, by charging specified amount of **ozone** into waste gas sampling system, and then absorbing and capturing this mixture gas in the hydrogen peroxide absorption liquid. CONSTITUTION:**Ozone** containing gas is charged into the waste gas sampling system at the **ozone** ratio, O3/(NOx+SOx), of more than 4, and NOx and SOx are sufficiently oxidized in the oxidation unit provided right after the sampling system to turn into **N2O5** and SO3. Then, this mixture gas is introduced into the absorption liquid containing hydrogen peroxide by more than 0.05 percent to obtain **nitric acid** and sulfuric acid respectively, which are absorbed and sampled simultaneously.

International (IPC 1-7): B01D53/34



Publication number	Publication date	Application number	Application date
1P55011033 A2	19800125	1P19780083694	19780710

1P19780083694 19780710

Assignee(s): (std): MITSUBISHI HEAVY IND LTD

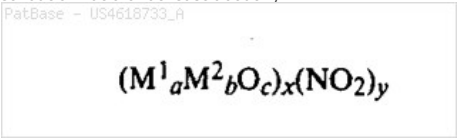
Inventor(s): (std) HAYASHI YUKIO : FURUSAWA TAKETOSHI

Title: VAPOR PHASE NITRATION OF AROMATIC COMPOUNDS

Abstract: Source: US4618733A Aromatic compounds are nitrated in the vapor phase via a process comprising contacting the aromatic compounds with a nitrating agent in the presence of a nitration promoting catalyst comprising the adduct of a Group 4b-Group 3b metal oxide composition represented by the empirical formula: (M₁aM₂bOc)_x(NO₂)_y wherein M₁ is at least one element selected from Group 4b of the Periodic Table of the Elements, M₂ is at least one element selected from Group 3b of the Periodic Table of the Elements, a is 1, b is 0 to 20, c is a number taken to satisfy the average valences of M₁ and M₂ in the oxidation states in which they exist in the composition, x is 1, and y is 0 to c, and a catalytically effective amount of sulfur trioxide. Such catalysts are particularly effective to catalyze the vapor phase nitration of chlorobenzene and are characterized in such reaction by providing a para/ortho isomer distribution ratio of at least about 2/1.

Classifications:

International (IPC 8-9): B01J27/02 B01J27/04 B01J27/24 C07B31/00 C07B43/02 C07B61/00 C07C201/00 C07C201/08 C07C205/06 C07C205/12 C07C205/37 C07C67/00 (Advanced/Invention); B01J27/02 B01J27/04 B01J27/24 C07B31/00 C07B43/00 C07B61/00 C07C201/00 C07C205/00 C07C67/00 (Core/Invention)
International (IPC 1-7): B01J23/00 B01J27/02 B01J27/24 C07B43/02 C07B61/00 C07C201/06 C07C201/08 C07C205/06 C07C205/12 C07C76/02 C07C79/10 C07C79/12
CPC: C07B43/02 B01J27/24 C07C201/08
European: B01J27/24 C07B43/02 C07C201/08 C07C205/06 C07C205/12 C07C205/37
US: 260/688 502/200 502/216 502/302 502/303 502/308 502/349 502/351 568/927 568/937 568/939



Family:

Publication number	Publication date	Application number	Application date
CA1258666 A1	19890822	CA19850495257	19851113
DE3583284 D1	19910725	DE19853583284	19851113
EP0184569 A1	19860611	EP19850870157	19851113
EP0184569 B1	19910619	EP19850870157	19851113
JP1821858 C3	19940210	JP19850254619	19851113
JP5033097 B4	19930518	JP19850254619	19851113
JP61120643 A2	19860607	JP19850254619	19851113
US4618733 A	19861021	US19840671253	19841114
US4746642 A	19880524	US19840671359	19841114
US4757043 A	19880712	US19840671358	19841114

Priority:

US19840671253 19841114 US19840671358 19841114 US19840671359 19841114
CA19850495257 19851113

Probable Assignee: SOLUTIA INC

Assignee(s): (std): MONSANTO CO

Assignee(s): SOLUTIA INC ; MONSANTO COMPANY ; MONSANTO CO ST LOUIS MO US ; SOLUTIA SYSTEMS INC ; SCHUMACHER IGNATIUS ; ABLECO FINANCE LLC ; ABLECO FINANCE LLC AS COLLATERAL AGENT ; ABLECO FINANCE LLC COLLATERAL AGENT AS ; CPFILMS INC ; MONCHEM INC ; MONCHEM INT ; MONCHEM INT INC

Inventor(s): (std): IGUNATEIUSU SHIYAUMATSUHERU ; SCHUMACHER IGNATIUS

Inventor(s): SCHUMACHER IGNATIUS BALLWIN MISSOURI 63011 US ; IGUNATEIUSU SHAUMATSUHERU

Agent(s): MCFADDEN FINCHAM; OSLER HOSKIN AND HARCOURT LLP

Designated states: DE FR GB IT

Abstract: Source: US5266292A PC. No. PCT/GB91/01249 Sec. 371 Date Apr. 16, 1992 Sec. 102(e) Date Apr. 16, 1992 PCT Filed Jul. 15, 1991 PCT Pub. No. WO92/02451 PCT Pub. Date Feb. 20, 1992. Method of extracting dinitrogen pentoxide (**N2O5**) from its mixture in **nitric acid**, which consists of providing a solution of the mixture in an inert organic solvent, stripping out the **N2O5** from solution in a carrier gas stream containing **ozone**, and subsequently condensing the **N2O5** out of the gas stream by contact with further inert organic solvent. The presence of **ozone** suppresses the dissociation of the **N2O5** transferred to the gas stream into dinitrogen tetroxide (N2O4). In a preferred embodiment the stripping and absorbing steps take place continuously in adjacent stripping and absorbing columns respectively having organic solvent recirculating through each.

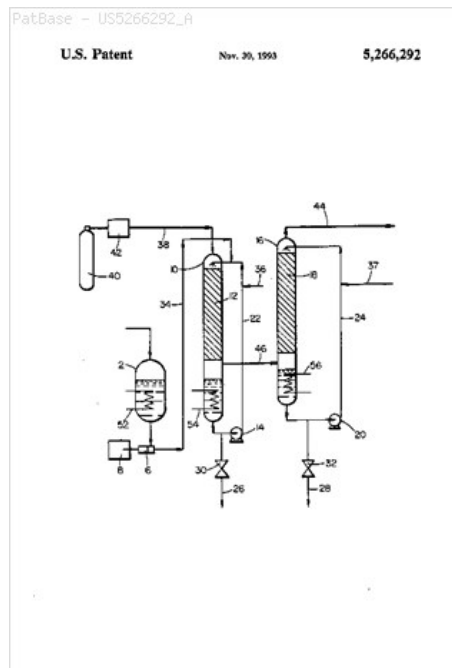
International (IPC 8-9): C01B21/00 C01B21/20 C01B21/46 (Advanced/Invention);
C01B21/00 (Advanced/Non-invention);
C01B21/00 (Core/Invention)

Internal (IPC 1-7): C01B21/00 C01B21/20 C01B21/22 C01B21/24 C01B21/38 C01B21/46

CPC: C01B21/206 C01B21/46

European: C01B21/20B C01B21/46

US: 423/235 423/390.1 423/400



Publication number	Publication date	Application number	Application date
AT120156 E	19950415	AT19910914014T	19910725
AU199183057 A1	19920302	AU19910083057	19910725
AU643317 B2	19931111	AU19910083057	19910725
BRPI9105855 A	19920825	BR1991PI05855	19910725
CA2066030 AA	19920327	CA19912066030	19910725
DE69108376 D1	19950427	DE19916008376	19910725
DE69108376 T2	19950907	DE19916008376T	19910725
DK0496853 T3	19950606	DK19910914014T	19910725
EP0496853 A1	19920805	EP19910914014	19910725
EP0496853 B1	19950322	EP19910914014	19910725
ES2070504 T3	19950601	ES19910914014T	19910725
FI921479 A	19920403	FI19920001479	19920403
FI921479 A0	19920403	FI19920001479	19920403
GB2252552 A1	19920812	GB19920005930	19920316
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IE68246 B	19960612	IE19910002732	19910801
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IL99016 A0	19920715	IL19910099016	19910730
IL99016 A1	19960119	IL19910099016	19910730
IN184822 A	20000930	IN1991DE00701	19910731
JP5501704 T2	19930402	JP19910513433T	19910725
MX9100510 A1	19920401	MX19910000510	19910802
NO921283 A	19920402	NO19920001283	19920402
NO921283 A0	19920402	NO19920001283	19920402
US5266292 A	19931130	US19920847989	19920416
WO202451 A1	19920220	WO1991GB01249	19910725

GB19900017135 19900804 WO1991GB01249 19910725

Assignee(s): (std): SECR DEFENCE BRIT : SEC DEP FOR DEFENCE IN THE UNI : SECR DEFENCE

Assignee(s): SEC DEP FOR DEFENCE IN UNI ; ARBER ANTHONY WILLIAM ; BAGG GREVILLE EUAN GORDON ; SEC DEP DEFENCE IN HM S GOVERNMENT OF UK OF GB AND N IREL ; SEC DEP FOR DEFENCE ; SEC DEP FOR DEFENCE IN HER BRITANNIC MAJESTY S GOV ; SEC DEP FOR DEFENCE IN HER BRITANNIC MAJESTY S GO ; SEC DEP FOR DEFENCE IN HER BRITANNIC MAJESTY S GOV ; SEC DEP FOR DEFENCE IN HER BRITANNIC MAJESTY S GOVERNMENT OF UNITED KINGDOM OF GREAT BRITAIN AND NORTHERN IRELAND ; SEC DEP FOR DEFENCE IN HER BRITANNI ; SEC DEP FOR DEFENCE IN HER BRITANNIC MAJESTY S GOVERNMENT OF UNITED KINGDOM OF GREAT BRITAIN AND NORTHERN ; SEC DEP FOR DEFENCE IN HER BRITANNIC MAJESTY S GOVERNMENT OF UNITED KINGDOM OF GREAT BRITAIN AND NORTHERN IRELAND ; SEC DEP FOR DEFENCE IN HER BRITANNIC MAJESTY S GOVE ; THE SECRETARY OF STATE FOR DEFENCE ; SECRETARY OF STATE FOR DEFENCE THE ; THE SECRETARY OF STATE FOR DEFENCE IN HER BRITANNIC MAJESTY S GOVERNMENT OF THE UNITED KINGDOM OF GREAT BRITAIN AND NORTHERN ; THE SECRETARY OF STATE FOR DEFENCE IN HER BRITANNIC MAJESTY S G ; THE SECRETARY OF STATE FOR DEFENCE IN HER BRITANNIC MAJESTY S GOVERNMENT ; SECRETARY OF STATE FOR DEFENCE IN HER BRITANNIC MAJESTY S GOVERNMENT OF THE UNITED KINGDOM OF GREAT BRITAIN AND NORTHERN IRELAND THE ; SECRETARY OF STATE FOR DEFENCE IN HER BRIT MAJESTY S GOVERNMENT OF UNITED KINGDOM GB AND N IRELAND ; THE SECRETARY OF STATE FOR DEFENCE IN HER BRITANNIC MAJESTY S GOVERNMENT OF THE UNITED KINGDOM OF GREAT BRITAIN AND NORTHERN IRELAND : THE SECRETARY OF STATE FOR DEFENCE IN HER BRITANNIC

MAJESTY S GOVE ; THE SECRETARY OF STATE FOR DEFENCE IN HER BRITANNIC MAJESTY S GOVERNMENT OF THE UNITED KINGDOM OF GR ; THE SECRETARY OF STATE FOR DEFENCE IN HER BRITANNIC MAJESTY S GOVERNMENT OF THE UNITED KINGDOM OF GB ; THE SECRETARY OF STATE FOR DEFENCE IN HER BRITANNIC MAJESTY S GOVERNMENT OF THE UNITED KINGDOM ; THE SECRETARY OF STATE FOR DEFENCE IN HER BRITANNIC MAJESTY S GOVERNMENT OF THE UNITED KINGDOM OF GREAT BRITAIN AND NORTHERN IRELAND WHITEHALL LONDON GB ; THE SECRETARY OF STATE FOR DEFENCE IN HER BRITANNIC MAJESTYS GOVERNMENT OF THE UNITED KINGDOM OF GREAT BRITAIN AND NORTHERN IRELAND ; THE SECRETARY OF STATE FOR DEFENCE OF THE UNITED KINGDOM

Inventor(s): (std): ARBER ANTHONY WILLIAM HURST DR ; ARBER WILLIAM ANTHONY ; BAGG GORDEN EUN GREVILLE ; BAGG GREVILLE ; BAGG GREVILLE E G ; BAGG GREVILLE EUAN ; BAGG GREVILLE EUAN GORDEN ; BAGG GREVILLE EUAN GORDON ; ARBER ANTHONY ; ARBER ANTHONY W ; ARBER ANTHONY WILLIAM ; BAGG GREVILLE EUAN GORDON MONK

Inventor(s): GREVILLE EUAN GORDEN BAGG ; GREVILLE EUAN GORDON BAGG ; BAGG GREVILLE EUAN GORDON 77 MONKSWOODAVENUE ESSEX ; ARBER ANTHONY WILLIAM 83 HURST DRIVE HERTFORDSHIRE ; ARBER ANTHONY WILLIAM 83 HURST DRIVE ; ARBER ANTHONY WILLIAM 83 HURST DRIVE HERTFORDSHIRE EN8 8DH GB ; BAGG GREVILLE EUAN GORDON 77 MONKSW ; BAGG GREVILLE EUAN GORDON 77 MONKSWOOD AVENUE ; BAGG GREVILLE EUAN GORDON 77 MONKSWOODAVENUE ESSEX EN9 1LD GB ; ANTHONY WILLIAM ARBER

Agent(s): DAVIES COLLISON CAVE; FETHERSTONHAUGH AND CO; EITAN PEARL LATZER AND COHEN ZEDEK

Designated states: AT AU BB BE BG BR CA CH DE DK ES FI FR GB GR HU IT JP KP KR LI LK LU MC MG MW NL NO PL RO SD SE SU US

Title: How to extract nitrogen renal site of Phe ?? quantity of material with a mixture of nitric acid. (Machine translation)

Abstract: Source: TH10843A

Machine translation: . How to extract the nitrogen oxides Mai Pae (N2O5) from a mixture of nitric acid, which is composed of. Providing a solution of the mixture in the inert organic solvent to remove it from the solution of N2O5 in the gas branch. Carrier gas containing the ozone. Next, condensation, and N2O5 from the gas stream with an inert organic solvent. To stop the breakdown of ozone transferred to N2O5. Stream of nitrogen gas into the Ettra oxide (N2O4) in the form that the process of elimination and absorption takes place continuously. Column to remove and absorb a contiguous sequence that has to do. A soluble organic flow through each column..

Classifications:
International (IPC 1-7): C01B21/20

Family:

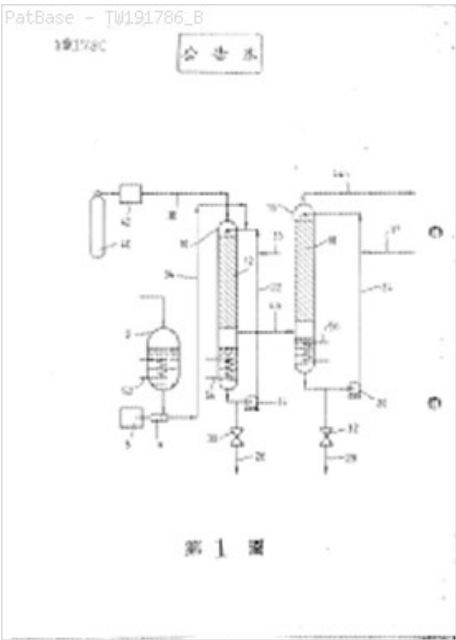
Publication number	Publication date	Application number	Application date
TH10843 A	19920401	TH19911001132	19910802

Title: With the **nitric acid** the nitric anhydride the method which the extract leaves from its mix (Machine translation)

Abstract: Source: TW191786B

Machine translation: **(N2O5)** comes out the method from the nitric anhydride mixture of with in the **nitric acid** the **N2O5** extract including to prepare first dissolves in the inert organic solvent the mixture solution, as soon as then in contains the **ozone** to carry delivers the gas to flow the stripping comes out **N2O5** from the solution, but finally further again flows with the inert organic solvent contact **N2O5** from the gas the condensation to come out. The **ozone** existence may suppress shifts flows to the gas **N2O5** to dissociate the nitrogen tetroxide (N2O4). In a good implementation example, the stripping and the absorption step are in neighboring and have the organic solvent separately in the stripping and the absorption tower which circulates in during carry on continuously.

Classifications:
International (IPC 8-9): C01B21/46 (Advanced/Invention);
C01B21/46 (Core/Non-invention)
International (IPC 1-7): C01B21/46



Family:

Publication number	Publication date	Application number	Application date
TW191786 B	19921001	TW19920101247	19920220

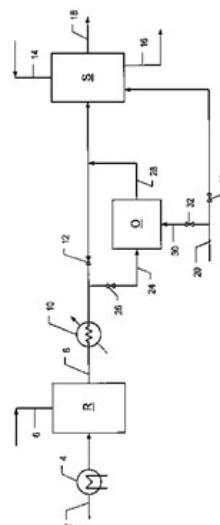
Probable Assignee: ROBERT WILLIAM BECKHAM

Assignee(s): ROBERT WILLIAM BECKHAM

Abstract: Source: US6197268B Nitrogen oxides are removed from a waste gas stream by contacting the waste gas stream with ammonia, thereby reducing the nitrogen oxides to nitrogen. Residual nitrogen oxides and unreacted ammonia in the waste gas stream leaving the nitrogen oxides reducing step are oxidized to nitrogen pentoxide or nitric acid by contacting this gas stream with ozone. Contact of the ozone and waste gas is preferably carried out in the presence of an aqueous solution at a pH above about 9 and at a temperature above about 75 Degrees Centigrade, and this step is preferably carried out in the presence of an ammonia-oxidizing catalyst.

European: B01D53/56 B01D53/75 B01D53/86F2
US: 422/325 422/326 1 422/302 422/303 422/304 2

US 6,197,268 B1



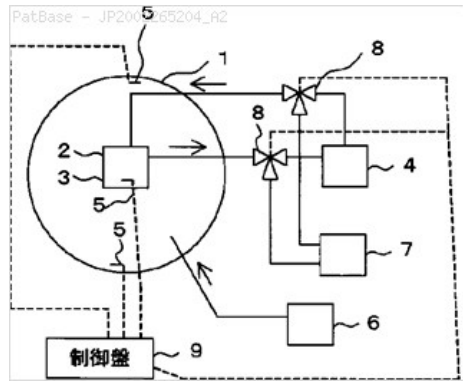
Publication number	Publication date	Application number	Application date
AT277680 E	20041015	AT20000305608T	20000703
AU200043790 A5	20010104	AU20000043790D	20000630
AU764628 B2	20030828	AU20000043790	20000630
AU764628 C	20040506	AU20000043790	20000630
CA2312652 AA	20010102	CA20002312652	20000628
CA2312652 C	20080916	CA20002312652	20000628
DE60014248 D1	20041104	DE20006014248	20000703
EP1064981 A1	20010103	EP20000305608	20000703
EP1064981 B1	20040929	EP20000305608	20000703
JP2001025646 A2	20010130	JP20000193793	20000628
JP4512238 B2	20100728	JP20000193793	20000628
NZ505573 A	20011130	NZ20000505573	20000630
US6197268 BA	20010306	US19990347316	19990702
ZA200003249 A	20010117	ZA20000003249	20000628

Designated states: AT BE CH CY DE DK ES FI FR GB GR IE IT LI LU MC NL PT SE

Title: OZONE GENERATING APPARATUS AND ITS HANDLING METHOD

Abstract: Source: JP2002265204A PROBLEM TO BE SOLVED: To provide an ozone generating apparatus in whose tank the generation of a toxic substance such as nitric acid and whose corrosion are prevented by mixing gaseous nitrogen in a gaseous starting material.SOLUTION: The ozone generating apparatus is provided with the tank 1 into which the gaseous starting material is introduced, an electric discharge part 2 disposed in the tank 1 for generating ozone by discharging electricity inside the gaseous starting material, a cooling fluid system 4 for cooling the part 2 when electricity is discharged, a heating fluid system 7 for heating the inside of the tank 1 to a temperature higher than the solidifying temperature of N₂O₅ and a changing-over means 8 for selecting the system 4 or the system 7.

Classifications:
International (IPC 8-9): C01B13/11 (Advanced/Invention);
C01B13/11 (Core/Invention)
International (IPC 1-7): C01B13/11



Family:

Publication number	Publication date	Application number	Application date
JP2002265204 A2	20020918	JP20010063464	20010307

Priority:
JP20010063464 20010307

Probable Assignee: TOSHIBA CORP
Assignee(s): (std): TOSHIBA CORP
Assignee(s): KABUSHIKI KAISHA TOSHIBA
Inventor(s): (std): KATAYAMA MASAHIRO