

Clarke, Mc
COLON

SUPERINTENDENCIA DE INDUSTRIA Y COMERCIO



Nº. 05-103104-00007-0000

Fecha: 2010-06-17 15:10:30 Dep. 2020 DIR.NUEVASCR
Tra. 11 PATENTEIYII Eve: 379 FASENACIONALII
Act. 444 RESPUESTAREQUE Folios: 4

P-675

SUPERINTENDENCIA DE INDUSTRIA Y COMERCIO
DIVISION DE NUEVAS CREACIONES
E. S. D.

Re: Expediente No. **05.103.104**

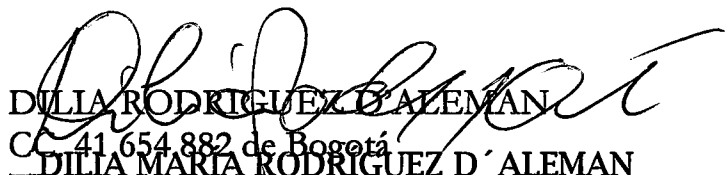
Solicitud de patente a nombre de **BOARD OF REAGENTS, THE UNIVERSITY OF TEXAS SYSTEM**

Yo, DILIA RODRIGUEZ D'ALEMAN, identificada como aparece al pie de mi firma, domiciliada en la carrera 11 No. 86-53, piso 6, obrando como apoderada de la sociedad **BOARD OF REAGENTS, THE UNIVERSITY OF TEXAS SYSTEM** domiciliada en Austin, Texas, Estados Unidos, solicitante de la patente de la referencia, en respuesta al oficio No. 06651 notificado por fijación en lista el 27 de mayo de 2010, me permito anexar las tasas oficiales que relaciono a continuación:

1. 10-45,235 de junio 2 de 2010 por \$175.000.00
2. 10-45,338 de junio 2 de 2010 por \$ 10.000.00
3. 10-36,805 de 6 de mayo de 2010 por \$2.000.00

Para un total de \$187.000.00 que corresponde al saldo dejado de pagar en la solicitud de examen de patentabilidad y se proceda al examen de fondo de la solicitud.

Señor Superintendente,


DILIA RODRIGUEZ D'ALEMAN
CC. 41.654.882 de Bogotá
DILIA MARIA RODRIGUEZ D' ALEMAN
TP 20824
CC. 41.654.882 de Bogotá.
Cód. 008
TP. 20824 CSJ

P-853

SUPERINTENDENCIA DE INDUSTRIA Y COMERCIO

NIT : 800176089-2

CERTIFICACION DE EXCEDENTE : 10 - 45,235
FECHA : JUNIO 2 DE 2010

SUPERINTENDENCIA DE INDUSTRIA Y COMERCIO



No. 05-103104- -00007-0000

Fecha: 2010-06-17 15:10:30 Dep. 2020 DIR.NUEVASCR
Tra. 11 PATENTEIYII Eve: 379 FASENACIONALII
Act. 444 RESPUESTAREQUE Folios: 4

***** CONSIGNACION *****

DEPOSITANTE	TIPO PAGO	BANCO	CUENTA	No. PAGO	FECHA PGO	Vr. PAGO
CLARKE MODET	CONSIGNACION	BANCO DE BOGOTA	062754387	134881294	02/06/2010	98,035,000.00

***** CONCEPTO *****

CANT.	RENTISTICO	CONCEPTO	TOTAL CONCEPTO
1	50005-01-09	OTROS SERVICIOS DE PROPIEDAD I	
		99 OTROS SERVICIOS ADMINISTRATIVOS	175,000.00
		TOTAL :	\$ 175,000.00

SON: CIENTO SETENTA Y CINCO MIL PESOS

RESPONSABLE : _____

RECIBO DE CAJA APLICADO AL EXPEDIENTE No. _____

ESTA CERTIFICACION DE EXCEDENTE DE PAGO SOLO PODRA SER UTILIZADA
COMO PARTE DE LA CANCELACION DE UNA TARIFA VIGENTE Y NO PODRA SER
SUSTITUIDA POR NINGUN RECIBO.

P-695

SUPERINTENDENCIA DE INDUSTRIA Y COMERCIO

NIT : 800176089-2

CERTIFICACION DE EXCEDENTE : 10 - 45,338
FECHA : JUNIO 2 DE 2010

SUPERINTENDENCIA DE INDUSTRIA Y COMERCIO



No. 05-103104- -00007-0000

Fecha: 2010-06-17 15:10:30 Dep. 2020 DIR.NUEVASCR
Tra. 11 PATENTEIYII Eve: 379 FASENACIONALII
Act. 444 RESPUESTAREQUE Folios: 4

***** CONSIGNACION *****

DEPOSITANTE	TIPO PAGO	BANCO	CUENTA	No. PAGO	FECHA PAGO	Vr. PAGO
CLARKE MODET	CONSIGNACION	BANCO DE BOGOTA	062754387	134881294	02/06/2010	98,035,000.00

***** CONCEPTO *****

CANT.	RENTISTICO	CONCEPTO	TOTAL CONCEPTO
1	50005-01-09	OTROS SERVICIOS DE PROPIEDAD I	
		99 OTROS SERVICIOS ADMINISTRATIVOS	10,000.00
		TOTAL :	\$ 10,000.00

SON: DIEZ MIL PESOS

RESPONSABLE : _____

RECIBO DE CAJA APLICADO AL EXPEDIENTE NO. _____

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SUSTITUIDA POR NINGUN RECIBO.

NIT : 800171000-2

253
CERTIFICACIÓN DE EXCEDENTE : 10 - 36,805
FECHA : MAYO 6 DE 2010

SUPERINTENDENCIA DE INDUSTRIA Y COMERCIO



No. 05-103104- -00007-0000

Fecha: 2010-06-17 15:10:30 Dep. 2020 DIR.NUEVASCR
Tra. 11 PATENTEIYII Eve: 379 FASENACIONALII
Act. 444 RESPUESTAREQUE Folios: 4

***** CONSIGNACION *****

DEPOSITO	TIPO PAGO	BANCO	CUENTA	No. PAGO	FECHA PAGO	Vr. PAGO
CLARKE Y CIA. COLOMBIA	CONSIGNACION	BANCO DE BOGOTA	062754387	353151680	05/05/2010	91,310,000.00

***** CONCEPTO *****

CANT.	CONCEPTO	TOTAL CONCEPTO
1	PRORROGAS Y RENOVACIONES	2,000.00
	TOTAL :	\$ 2,000.00

SON: DOS MIL PESOS

RESPONSABLE:

RECIBO DE PAGO APLICADO AL ASUNTO No.

ESTA CERTIFICACIÓN DE EXCEDENTE DE PAGO SOLO PODRA SER UTILIZADA
COMO PARTE DE LA CANCELACIÓN DE UNA TARIFA VIGENTE Y NO PODRA SER
SUSTITUIDA POR NINGUN RECIBO.

204
2007

SUPERINTENDENCIA DE INDUSTRIA Y COMERCIO
DIVISIÓN DE NUEVAS CREACIONES

2020
Bogotá, D. C., 14 de septiembre de 2010

Doctor
Dilia Rodríguez D'Alemán
Representante
Board of Regents, The University of Texas System

ASUNTO Radicación **05-103104**
 Trámite 002
 Evento 001
 Actuación 430
 Oficio 12058
 Folios 040

Patente de Invención ☒ Patente de Modelo de Utilidad ☐

Vía Nacional ☐

Vía PCT (fase nacional) ☒ Cap. I ☒ Cap. II ☐

No. Sol. Internacional **PCT/05/103104**
Fecha de Presentación Internacional 4 de marzo de 2004

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 le comunica:

1. Documentos estudiados

- 1.1. Descripción: Folios: 25 a 57 tal como se radicó inicialmente
 Folios 180 a 195 tal como se modificó el 18 de diciembre de 2009
- 1.2. Reivindicaciones: Folios 58 a 60 tal como se radicó inicialmente
 Folios 196 a 197 tal como se modificó el 18 de diciembre de 2009
- 1.3. Dibujos: Folios 62 a 63 tal como se radicó inicialmente
- 1.4. Prioridad: Cap. I ☐
- Fecha 10 de marzo de 2003
 País Estados Unidos
 Número 60/453279

2. Modificaciones (Artículo 34 D. 486 y Art. 22 Tratado PCT)

Se aceptan las modificaciones realizadas por el solicitante toda vez que no amplían el objeto inicial de la solicitud.

3. Objeto de la invención

- Título de la solicitud (folio 1)
Regeneración de una solución acuosa de un proceso de absorción de gas ácido mediante vaporización instantánea y separación con vapor en cuerpos múltiples
- Las reivindicaciones 1 a 15 de la solicitud en estudio se refieren a

Un método mejorado para extraer un gas ácido de una corriente gaseosa que lo contiene usando equipo de absorción acuosa y despojamiento, la mejora consiste en:

- (a) pasar la corriente de solvente rico en gas ácido que sale del equipo de absorción, a través de un despojador de presiones múltiples, en donde la corriente de solvente rico en gas ácido pasa por múltiples etapas de evaporación instantánea, de tal forma que el vapor obtenido por evaporar instantáneamente la corriente de solvente rico en gas ácido en cada cuerpo de evaporación instantánea, despoja el gas ácido de la corriente de solvente rico en gas ácido, resultando en una corriente gaseosa rica en gas ácido que sale del despojador de presiones múltiples; en donde el despojador de presiones múltiples es operado a múltiples niveles de presión, tal que el vapor obtenido en cada etapa de evaporación instantánea es comprimido en un compresor y alimentado a la etapa de evaporación instantánea previa a una presión mayor; y*
- (b) reciclar la corriente de solvente pobre en gas ácido que sale del despojador de presiones múltiples en el paso (a) de regreso al equipo de absorción, al menos una vez.*

Un equipo para despojar gas ácido de una corriente de solvente rica en gas ácido, el cual comprende:

- (a) una columna de despojamiento que comprende muchas etapas de evaporación instantánea; y*
- (b) al menos un compresor conectado entre cada una de las etapas de evaporación instantánea tal que el vapor producido en cada etapa de evaporación instantánea es comprimido y alimentado a la etapa de evaporación instantánea anterior a mayor presión.*

- El anterior procedimiento y el equipo que lo realiza buscan optimizar la extracción y recuperación de gases de carácter ácido
- La Clasificación Internacional de Patentes (IPC) para esta solicitud es **B 01 D 53/14.**

4. De la solicitud de Patente

4.1. Reivindicaciones (Artículo 30 D. 486)

El capítulo reivindicatorio de la solicitud en estudio presenta los siguientes defectos:

- *Es inaceptable el uso de expresiones ambiguas en un capítulo reivindicatorio. Cuando el solicitante refiere "muchas etapas", una persona que lea el texto no podrá delimitar lo que quiere decir el solicitante; por lo mismo, se deberán eliminar dichas expresiones.*

Por lo anterior, el capítulo reivindicatorio no cumple con el requisito de definición, claridad, concisión o sustento por la descripción de acuerdo al art. 30 de la Decisión 486.y/o art.22 Tratado PCT.

5. Determinación del Estado de la Técnica

- La fecha que se ha tenido en cuenta para determinar el estado de la técnica es 10 de marzo de 2003
- Teniendo en cuenta la fecha indicada se realizó la búsqueda en el estado de la técnica de documentos relacionados con la solicitud encontrándose los siguientes documentos más relevantes:

Nº	Documento	Título	Fecha de publicación*
D1	McCabe y otros	Operaciones Unitarias en Ingeniería Química	1991
D2	Perry y otros	Perry's chemical engineer's handbook	1999
D3	Treybal Robert	Operaciones de transferencia de masa	1980
D4	US 5 435 977	Acid gas removal system employing regenerator with internal flash selection	25,07,1995
D5	US 4 780 115	Process for removing undesirable component from gases	25,10,1988
D6	US 5145658	Reclaiming of heat of reaction energy from an alkaline scrubbing solution used in acid gas removal process and apparatus thereof	08,09,1992
D7	US 4 189 307	Production of clean HCN free synthesis gas	19,02,1980
D8	US 4 160 810	Removal of acid gases from hot gas mixtures	10,07,1979
D9	GB 1 484 050	Improvements to the processes for removing acid gases from gaseous mixtures	24,08,1977

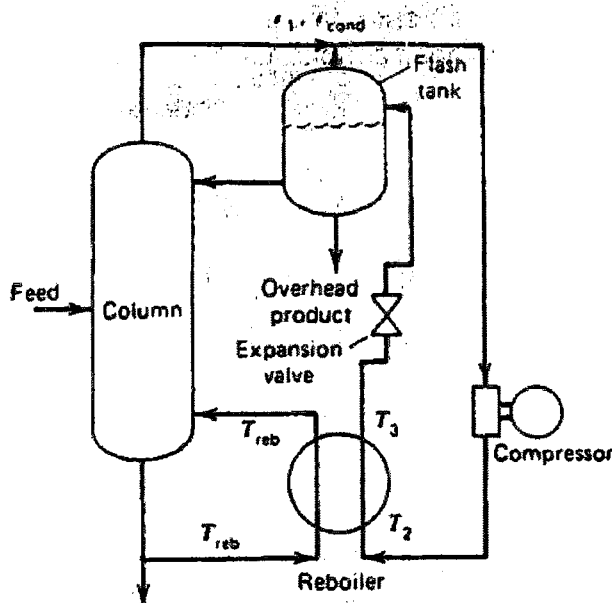
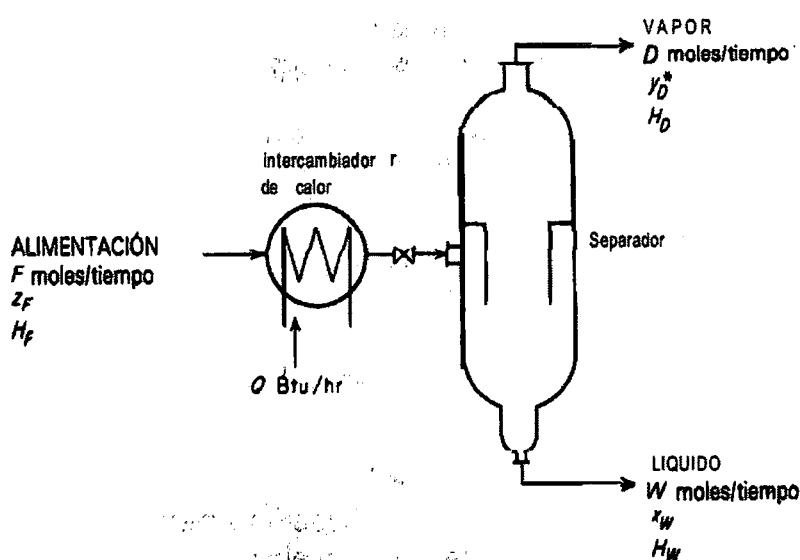
6. Análisis de patentabilidad (Artículo 14 D. 486)

El solicitante pretende que se le proteja un proceso para despojar a un solvente de un gas ácido empleando sucesivas evaporaciones instantáneas.

De acuerdo a lo observado, el solicitante refiere un proceso que enuncia principios básicos de la ingeniería. Así lo señalan las referencias D1, D2 y D3.

La destilación flash consiste en la vaporización de una fracción definida del líquido, en forma tal que el vapor que se forma está en equilibrio con el líquido residual, la separación del vapor y el líquido y la posterior condensación del líquido. Dentro de los

elementos básicos de un sistema de destilación flash, se encuentra siempre un medio para que se efectúe un cambio de presión en la alimentación de la solución al destilador. En la práctica, la mayoría de sistemas de desorción y destilación buscan configurar sistemas continuos de evaporaciones flash parciales; así lo enseña la teoría básica.



(d)

Ahora bien, toda operación binaria (de separación en este caso) se centra en las propiedades termodinámicas de la mezcla; por lo mismo, se deben tener presentes las propiedades con relación a la temperatura, presión, y en el caso de que algunas de ellas se mantengan constantes. En las páginas 13-25 y siguientes del documento D2, así como en D3 sección nueve, se refiere como se manejan dichas variables. Nótese como todos los métodos de cálculo se centran en establecer sucesivas evaporaciones flash.

Nótese como una de las posibles variantes de la metodología empleada comúnmente se basa en establecer diferentes presiones en diferentes partes y como la corriente pobre en la sustancia desorbida es reintegrada al proceso para que inicie un nuevo ciclo.

De todo lo anterior, se concluye que lo que el solicitante pretende proteger un conjunto de operaciones unitarias de empleo común en el arte, donde simplemente se le atribuye un uso específico en un solvente con gas ácido donde dicho gas busca desorberse.

Cómo se observa también, dicha metodología se ha empleado de forma continua a través de muchos años. Ejemplo de esto son los documentos D4 a D9, que si bien no contemplan exactamente el mismo proceso relacionado en la presente solicitud, cada uno de ellos incorpora los principios de desorción o destilación que contiene la evaporación flash o instantánea en al menos alguna de las operaciones unitarias de cada proceso de cada documento. Nótese que los equipos que relaciona el solicitante en la reivindicación 15 se desprenden de estos principios.

En conclusión, la presente solicitud refiere para su protección una serie de principios básicos muy conocidos en el arte acerca del despojamiento de un soluto partiendo de una solución, centrándose en el principio de la evaporación instantánea y de sucesivas etapas de la misma. Por consiguiente, la presente solicitud carece de los requisitos de altura inventiva necesarios para que se le conceda el privilegio solicitado.

7. Conclusión:

Los requisitos de patentabilidad de la presente solicitud se encuentran afectados así:

N°	Documento N°	Reivindicaciones afectadas	Requisito que afecta
D1	McCabe y otros	1 -15	Nivel inventivo
D2	Perry y otros	1 -15	Nivel inventivo
D3	Treybal Robert	1 -15	Nivel inventivo
D4	US 5 435 977	1 -15	Nivel inventivo
D5	US 4 780 115	1 -15	Nivel inventivo
D6	US 5145658	1 -15	Nivel inventivo
D7	US 4 189 307	1 -15	Nivel inventivo
D8	US 4 160 810	1 -15	Nivel inventivo
D9	GB 1 484 050	1 -15	Nivel inventivo

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 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.

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 N° 10 de 2001.

Álix Carmenza Céspedes de Vergel
Directora de Nuevas Creaciones (C)

Concepto Técnico No. **2963**

Examinador Técnico **202003**

El anterior requerimiento fue notificado por fijación en lista, de fecha 17 SET. 2010

MADRID, BUENOS AIRES, CARACAS, GUATEMALA, LIMA, MEXICO
NEW YORK, PANAMA, SAN JUAN, SANTIAGO DE LOS CABALLEROS, SAO PAULO,
PORT AU PRINCE, PORT-au-Prince, LISBON, BRISBANE, SYDNEY, MELBOURNE, AUCKLAND,
PERTH, WELLINGTON, DUNEDIN, CHRISTCHURCH, HAMILTON, ADELAIDE, SYDNEY, ST. LOUIS, TORONTO

Walter L. McCabe
North Carolina State University

Julius C. Smith
Cornell University

Peter Harriott
Cornell University

Exemple de la structure

Elia Guzmán Ferrando
Fernando Miranda Coronel
Carlos Negro Alvarez
Mercedes Oñet Pala
Francisco Rodríguez Somolinos

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Destilación **DIRECCIÓN** **DESTILACIÓN**

En la práctica, la destilación puede llevarse a cabo según dos métodos principales. El primer método se basa en la producción de vapor mediante la calefacción de la mezcla líquida que se desea separar y condensación de los vapores en un condensador que el líquido resulte al condensar. En este, no hay ningún tipo de movimiento en la mezcla líquida que se desea separar. En consecuencia, la destilación por ebullición se basa en el resque de una parte del componente a la columna, quedando en la columna la parte que no se evapora. Cuando se han separado los vapores que se desean extraer, el condensador se calienta y se hacen salir los vapores que se desean extraer. Cuando se han separado los vapores que se desean extraer, el condensador se calienta y se hacen salir los vapores que se desean extraer. Cuando se han separado los vapores que se desean extraer, el condensador se calienta y se hacen salir los vapores que se desean extraer.

Destilación flash

La destilación flash consiste en la vaporización de una fracción definida del líquido, en una forma tal que el vapor que se forma está en equilibrio con el líquido residual, la separación del vapor y el líquido, y posterior condensación del vapor. La Figura 18.1 muestra los elementos de un sistema de destilación flash. La alimentación se hace circular, por medio de la bomba A, a través del calentador B, y se reduce la presión en la válvula C. Una salida medida de vapor y líquido entra en el separador D, en el que permanece suficiente tiempo para que se separen las corrientes de líquido y vapor. Debido al gran contacto existente entre el líquido y el vapor antes de su separación, las corrientes que salen de ambos están en equilibrio. El vapor sale a través de la línea E y el líquido a través de la línea F.

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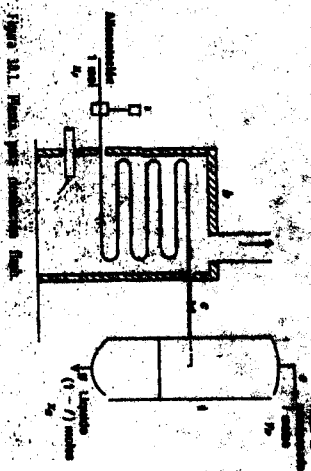


Figura 18.1. Planta para destilación flash.

DESTILACIÓN 59

La destilación flash se realiza a gran escala en el refinado del petróleo, donde la función de separar los componentes en corrientes líquidas y el fluido caliente se encarga a una destilación flash para obtener un vapor de carbon y un líquido residual, considerando ambos corrientes pueden ser aprovechadas.

$$x_2 = fD_2 + (1 - f)D_1 \quad (18.1)$$

En la Ecuación (18.1) hay las dos incógnitas x_2 e y_2 . Para resolver la ecuación es preciso disponer de una relación entre las incógnitas. Tal relación viene dada por la curva de equilibrio, en la que y_2 y x_2 son las coordenadas de un punto de esta curva. Si x_2 e y_2 se sustituyen por z e y , respectivamente, la Ecuación (18.1) puede escribirse así:

$$y = \frac{1 - f}{f} x + \frac{x_2}{f} \quad (18.2)$$

1 La destilación flash se realiza a gran escala en el refinado del petróleo, donde la función de separar los componentes en corrientes líquidas y el fluido caliente se encarga a una destilación flash para obtener un vapor de carbon y un líquido residual, considerando ambos corrientes pueden ser aprovechadas.

32 OPERACIONES UNITARIAS DE INGENIERIA QUIMICA

La función f es cualquier función matemática que depende de la entalpía del líquido caliente que entra y de las entalpías del líquido y el vapor que salen de la columna de flash. Para una condición dada de la alimentación, la función f puede mantenerse operando a una presión menor.

La Ecuación (18.2) es la ecuación de una recta de pendiente $-(1-f)/f$ y que puede representarse sobre el diagrama de equilibrio. Las coordenadas de la intersección de esta recta y la línea de equilibrio son $x = x_D$ y $y = y_D$. La intersección de esta línea del balance de materia y la línea diagonal $x = y$ resulta conveniente para ser utilizada como un punto de dicha línea. Tomando $x = x_D$ en la Ecuación (18.2), se obtiene

$$y = -\frac{1-f}{f}x_D + \frac{x_D}{f}$$

de donde $y = x_D = x$. La línea del balance de materia coincide con la diagonal en $x = x_D$ para todos los valores de f .

Ejemplo 18.1. Una mezcla de 50 moles por 100 de benceno y 50 moles por 100 de tolueno se somete a destilación flash completa con una presión en el evaporador de 1 atm. En la Figura 18.2 y 18.3 se representan la curva del equilibrio para benceno-tolueno.

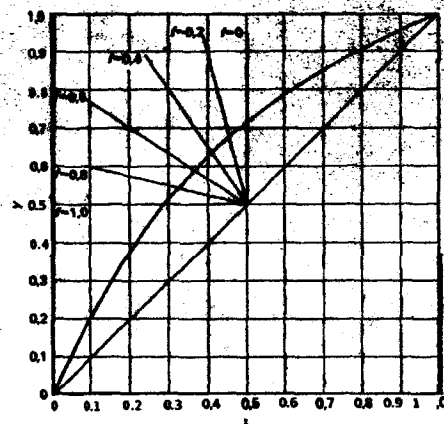


Figura 18.2. Curva de equilibrio del sistema benceno-tolueno. Construcción gráfica para el Ejemplo 18.1.

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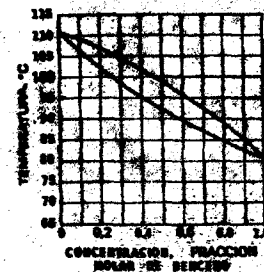


Figura 18.3. Diagrama de puntos de ebullición para el sistema benceno-tolueno a 1 atm.

Diagrama del punto de ebullición. Represente las siguientes variables en función de f , la fracción de vaporización: (a) la temperatura en el evaporador, (b) la composición del líquido que sale del evaporador, (c) la composición del vapor que sale del evaporador.

Solución:

Para cada uno de los distintos valores de f se calcula los correspondientes valores de $-(1/f)-1$. Utilizando estos valores como pendientes se traza una serie de rectas que pasan a través del punto (x_D) de la curva de equilibrio de la Figura 18.2. Esta línea corta a la curva de equilibrio en los valores correspondientes a x_D y y_D . La temperatura de cada evaporador se obtiene leyendo a partir de la Figura 18.3. Los resultados se muestran en la Figura 18.1 y se representan en la Figura 18.4. Las líneas correspondientes a 0 y 100 por 100 de vaporización son las líneas de budo y de vado, respectivamente.

Tabla 18.1. Datos para el Ejemplo 18.1

Fracción vaporizada f	Pendiente $-\frac{1-f}{f}$	Concentración, fracción molar de C_6H_6		Temperatura, °C
		Líquido x_D	Vapor y_D	
1	0	0.50	0.71	92.2
0.2	-4	0.68	0.67	93.7
0.4	-1.5	0.41	0.63	96.0
0.6	-0.67	0.36	0.66	96.5
0.8	-0.25	0.32	0.54	97.7
1.0	0	0.29	0.50	99.0

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Distillation

[illegible]

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The *lighter* (lower-boiling) components tend to concentrate in the vapor phase, while the *heavier* (higher-boiling) components tend to remain in the liquid phase. The result is a vapor phase that becomes richer in light components as it passes up the column and a liquid phase that becomes richer in heavy components as it descends downward. The overall separation achieved between the distillate and the bottom product depends primarily on the *relative volatilities* of the components, the number of contacting trays, and the ratio of the liquid-to-vapor flow rate to the vapor phase flow rate.

Use of the equilibrium-stage concept separates the design of a distillation column into three major steps: (1) Thermodynamic data and methods needed to predict equilibrium-phase compositions are assembled. (2) The number of equilibrium stages required to accomplish a specified separation, or the separation that will be accomplished in a given number of equilibrium stages, is calculated. (3) The number of stages and number of equilibrium stages is calculated. The number of stages is converted to an equivalent number of actual contact trays or height of packing, and the column diameter is determined. Much of the third step is eliminated if a rate-based model is used. This section deals primarily with the second step. Section 14 covers the third step. Section 3 and 4 cover the first step, but a summary of methods and some useful data are included in this section.

All separation operations require energy input in the form of heat or work. In the conventional distillation operation, as typified in Fig. 13-1, energy required to separate the species is added to the form of heat at the reboiler at the bottom of the column, where the temperature is highest. Also, heat is removed from a condenser at the top of the column, where the temperature is lowest. This frequently results

CONTINUOUS-DISTILLATION OPERATIONS 13-5

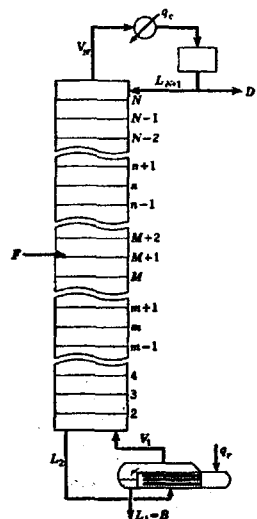


FIG. 13-1 Schematic diagram and nomenclature for a simple distillation column with one feed, one total overhead condenser, and a partial reboiler.

large energy-input requirements and low overall thermodynamic efficiency, when the heat removed in the condenser is wasted. Complex distillation operations that offer higher thermodynamic efficiency and lower energy-input requirements have been under intense investigation. In some cases, all or a portion of the energy input is as work.

Complex distillation operations may utilize single columns, as shown in Fig. 13-2 and discussed by Peterson and Wells [Chem. Eng., 84(20), 75 (Sept. 26, 1977)], Nafi [Chem. Eng. Prog., 73(7), 58 (1979)], and Branan and Marple [Am. Inst. Chem. Eng. Symp. Ser. 76, 192, 10 (1980)], or two or more columns that are thermally linked as shown in Figs. 13-3 and 13-6 and discussed by Peterson and Wells (op. cit.) and Mah, Nicholas, and Wodnik [Am. Inst. Chem. Eng. J., 23, 651 (1977)].

In Fig. 13-3a, which is particularly useful when a large temperature difference exists between the ends of the column, interreboilers add heat at lower temperatures and/or intercondensers remove heat at higher temperatures. As shown in Fig. 13-3b, these intermediate heat exchangers may be coupled with a heat pump that takes energy from the intercondenser and uses shaft work to elevate this energy to a temperature high enough to transfer it to the interreboiler.

Particularly when the temperature difference between the ends of the column is not large, any of the three heat-pump systems in Fig. 13-3c, d, and e that involve thermal coupling of the overhead condenser and bottoms reboiler might be considered to eliminate external heat transfer almost entirely, substituting shaft work as the prime energy input for achieving the separation. More complex arrangements are considered by Björn, Grén, and Ström [Chem. Eng. Process., 29, 185 (1991)]. Alternatively, the well-known multiple-

column or split-tower arrangement of Fig. 13-3d, which corresponds somewhat to the energy-saving concept employed in multi-effect evaporation, might be used. The feed is split more or less equally among columns that operate in parallel, but at different pressures, in a cascade that decreases from left to right. With proper selection of column operating pressure, this permits the overhead vapor from the higher-pressure column to be condensed in the reboiler of the lower-pressure column. External heat-transfer media are needed only for the reboiler of the first effect and the condenser of the last effect. Thus, for N effects, utility requirements are of the order $1/N$ of those for a conventional single-effect column. Wankat [Ind. Eng. Chem. Res., 33, 884 (1993)] develops a large number of more complex multi-effect schemes, some of which show significant reduction in energy requirements.

In another alternative shown in Fig. 13-3b, the rectifying section may be operated at a pressure sufficiently higher than that of the stripping section such that heat can be transferred between any desired pairs of stages of the two sections. This technique, described by Mah et al. (op. cit.) and referred to as SRV (secondary reflux and vaporization) distillation, can result in a significant reduction in utility requirements for the overhead condenser and bottoms reboiler.

When multicomponent mixtures are to be separated into three or more products, sequences of simple distillation columns of the type shown in Fig. 13-1 are commonly used. For example, if a ternary mixture is to be separated into three relatively pure products, either of the two sequences in Fig. 13-4 can be used. In the direct sequence, shown in Fig. 13-4a, all products but the heaviest are removed one by one as distillates. The reverse is true for the indirect sequence, shown in Fig. 13-4b. The number of possible sequences of simple distillation columns increases rapidly with the number of products. Thus, although only the 2 sequences shown in Fig. 13-4 are possible for a mixture separated into 3 products, 14 different sequences (one of which is shown in Fig. 13-5) can be synthesized when 5 products are to be obtained.

As shown in a study by Tadder and Rudd [Am. Inst. Chem. Eng. J., 24, 303 (1978)], conventional sequences like those of Fig. 13-4 may not always be the optimal choice, particularly when species of intermediate volatility are present in large amounts in the feed or need not be recovered at high purity. Of particular interest are thermally coupled systems. For example, in Fig. 13-5a, an impure vapor sidestream is withdrawn from the first column and purified in a side-cut rectifier, the bottoms of which is returned to the first column. The thermally coupled system in Fig. 13-5b, discussed by Strapi and Lockhart [Chem. Eng. Prog., 68(10), 71 (1972)] and referred to as Fillyk tower, is particularly useful for reducing energy requirements when the initial feed contains close-boiling species. Shown for a ternary feed, the first column in Fig. 13-5b is a prefractionator, which sends essentially all of the light component and heavy component to the distillate and bottoms respectively, but permits the component of intermediate volatility to be split between the distillate and bottoms. Products from the prefractionator are sent to appropriate feed trays in the second column, where all three products are produced, the middle product being taken off as a sidestream. Only the second column is provided with condenser and reboiler; reflux and boil-up for the prefractionator are obtained from separations that produce more than three products. Procedures for the optimal design of thermally coupled systems are presented by Tsionas/Tou and Smith [Trans. I. Chem. E., 70, Part A, 118 (1992)]. A scheme for combining thermal coupling with heat pumps is developed by Agrawal and Yee [Ind. Eng. Chem. Res., 33, 2717 (1994)].

RELATED SEPARATION OPERATIONS

The simple and complex distillation operations just described all have two things in common: (1) both rectifying and stripping sections are provided so that a separation can be achieved between two components that are adjacent in volatility; and (2) the separation is effected only by the addition and removal of energy and not by the addition of any mass separating agent (MSA) such as in liquid-liquid extraction.

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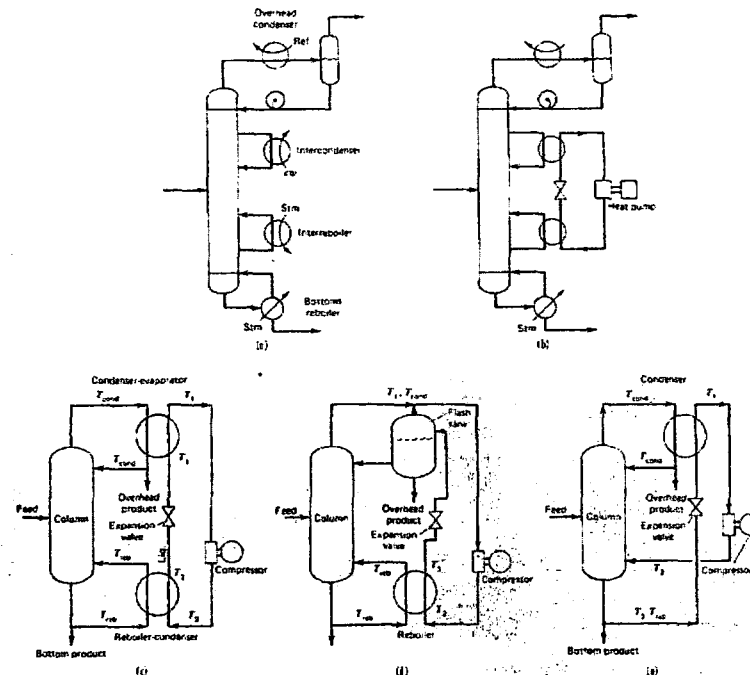


FIG. 13-2 Complex distillation operations with single columns: (a) Use of intermediate heat exchangers; (b) Coupling of intermediate heat exchangers with heat pump; (c) Heat pump with external refrigerant; (d) Heat pump with bottom reboiling.

Sometimes alternative single- or multiple-stage vapor-liquid separation operations of the types shown in Fig. 13-7, may be more suitable than distillation for the specified task.

A single-stage flash, as shown in Fig. 13-7a, may be appropriate if (1) the relative volatility between the two components to be separated is very large; (2) the recovery of only one component, without regard to the separation of the other component, in one of the two product streams is to be achieved; or (3) only a partial separation is to be made. A common example is the separation of light gases such as hydrogen and methane from aromatics. The desired temperature and pressure of a flash may be established by the use of heat exchangers, a valve, a compressor, and/or a pump upstream of the vessel used to separate the product vapor and liquid phases. Depending on the original condition of the feed, it may be partially condensed or partially vaporized in a so-called flash operation.

If the recovery of only one component is required rather than a sharp separation between two components of adjacent volatility,

absorption or stripping in a single section of stages may be sufficient. If the feed is vapor at separation conditions, absorption is used either with a liquid MSA absorbent of relatively low volatility as in Fig. 13-7b or with reflux produced by an overhead partial condenser as in Fig. 13-7c. The choice usually depends on the ease of partially condensing the overhead vapor or of recovering and recycling the absorbent. If the feed is liquid at separation conditions, stripping is used, either with an externally supplied vapor stripping agent of relatively high volatility as shown in Fig. 13-7d or with boil-up produced by a partial reboiler as in Fig. 13-7e. The choice depends on the ease of partially reboiling the bottoms or of recovering and recycling the stripping agent.

If a relatively sharp separation is required between two components of adjacent volatility, but either an undesirably low temperature is required to produce reflux at the column operating pressure or an undesirably high temperature is required to produce boil-up then refluxed stripping as shown in Fig. 13-7f or reboiled absorption

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CONTINUOUS DISTILLATION OPERATIONS 13-7

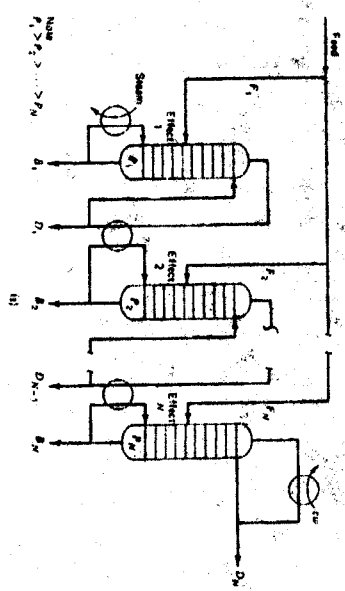
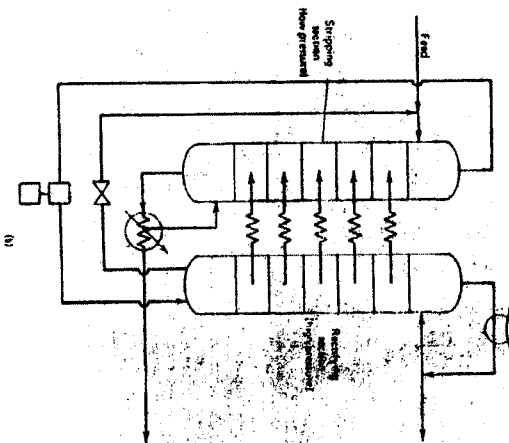


FIG. 13-3. Simple distillation operations with two or more columns. (a) Multistage distillation; (b) SIV distillation.



13-8 DISTILLATION

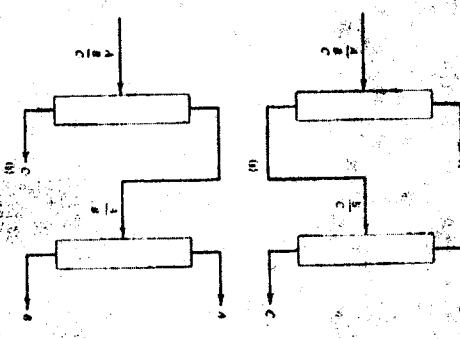


FIG. 13-4. Distillation sequence for the separation of three components. (a) Direct sequence; (b) indirect sequence.

FIG. 13-4. Out of 14 different sequences for the separation of 3 components, 2 are the most efficient.

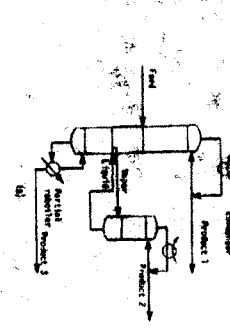
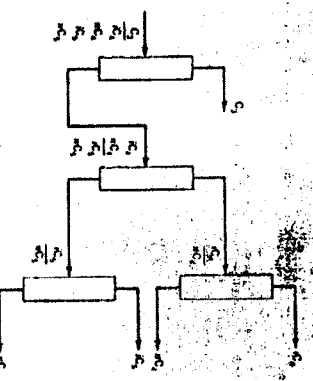
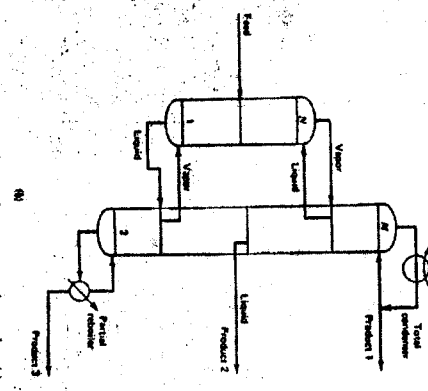


FIG. 13-4. Thermally coupled system for separation into three products. (a) Feed preheated by vapor condenser and side reboiler; (b) Feed preheated by vapor condenser.



is shown in Fig. 13-7 may be used in either case, the choice of which is determined by the nature of the feed and the nature of the products. When the volatility difference between the two components to be separated is so small that a very large number of stages would be required, then extractive distillation, as shown in Fig. 13-8, should be considered. Here, an MSA is selected that increases the volatility difference sufficiently to make the large required number of stages economically feasible. The MSA is then separated from the mixture of low volatility components in the bottom, from which it is recovered and recycled. It is introduced in an appreciable amount near the top stage of the column so as to effect the volatility difference over most of the stages. Some refer to the top stage as utilized to introduce the MSA entrainer in the distillation. An alternative to extractive distillation is azeotropic distillation, which is shown in Fig. 13-9. In this process, an azeotropic mixture, an MSA that forms a heterogeneous azeotrope, is added to the feed. The azeotrope is then separated from the mixture, and the MSA is recovered and recycled.

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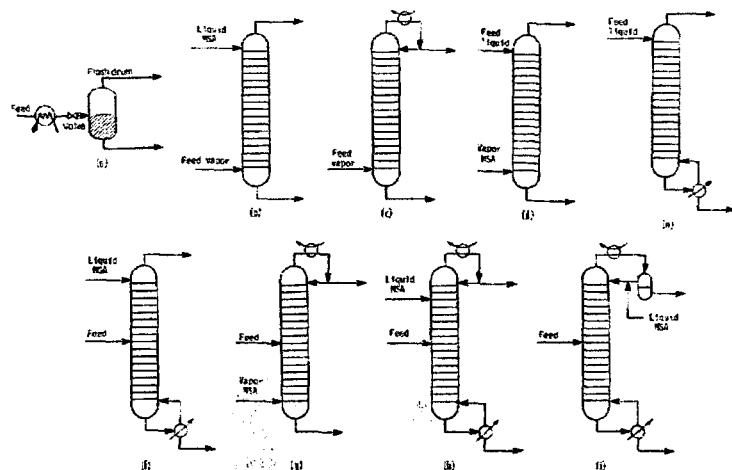


FIG. 13-7 Separation operations related to distillation. (a) Flash vaporization or partial condensation. (b) Absorption. (c) Rectifier. (d) Stripping. (e) Reboiled stripping. (f) Reboiled absorption. (g) Refluxed stripping. (h) Extractive distillation. (i) Azeotropic distillation.

noting azeotrope with one or more components of the feed is utilized. The azeotrope is taken overhead, and the MSA-rich phase is decanted and returned to the top of the column as reflux.

Numerous other multistaged configurations are possible. One important variation of a stripper, shown in Fig. 13-7d, is a refluxed stripper, in which an overhead condenser is added. Such a configuration is sometimes used to steam-strip sour water containing NH_3 , H_2O , phenol, and HCN.

All the separation operations shown in Fig. 13-7, as well as the simple and complex distillation operations described earlier, are referred to here as distillation-type separations because they have much in common with respect to calculations of (1) thermodynamic properties, (2) vapor-liquid equilibrium stages, and (3) column sizing. In fact, as will be evident from the remaining treatment of this section, the trend is toward single generalized digital-computer-program packages that compute many or all distillation-type separation operations.

This section also includes a treatment of distillation-type separations from a rate-based point of view that utilizes principles of mass transfer and heat transfer. Section 14 also presents details of that subject as applied to absorption and stripping.

SYNTHESIS OF MULTICOMPONENT SEPARATION SYSTEMS

The sequencing of distillation columns and other types of equipment for the separation of multicomponent mixtures has received much attention in recent years. Although one separator of complex design can sometimes be devised to produce more than two products, more

often a sequence of two-product separators is preferable. Often, the sequence includes simple distillation columns. A summary of sequencing methods, prior to 1977, that can lead to optimal or near-optimal designs, is given by Henley and Seader [op. cit.]. More recent methods for distillation-column sequencing are reviewed by Modai and Westerberg [Ind. Eng. Chem. Res., 31, 538 (1992)], who also present a more generally applicable method based on a marginal prior that is the change in price of a separation operation when the separation is carried out in the absence of nonkey components. The synthesis of sequences that consider a wide range of separation operations is a knowledge-based approach is given by Burdick and Parr for liquid mixtures [Ind. Eng. Chem. Res., 29, 421 (1990)] and for gas-vapor mixtures [Ind. Eng. Chem. Res., 31, 1679 (1992)]. A knowledge-based method is also given by Sheppard, Beltrami, and Motard [Chem. Eng. Comm., 106 (1991)] for the synthesis of distillation sequences that involve nonsharp separations where nonkey components distribute. The problem-decomposition approach of Wahschoff, Le Rudulier, and Westerberg [Ind. Eng. Chem. Res., 32, 1124 (1993)] is directed to the synthesis of complex separation sequences that involve nonsharp splits and recycle, including azeotropic distillation. The method is applied using a computer-aided separation process designer called SPLIT. An expert system, called EXSEP, for the synthesis of solvent-based separation trains is presented by Brunet and Liu [Ind. Eng. Chem. Res., 33, 315 (1994)]. The use of ternary-composition diagrams and residue-curve maps, of the type so popular by Doherty and coworkers, is reviewed and evaluated for application to the synthesis of complex separation sequences by Finn and Liu [Ind. Eng. Chem. Res., 33, 2506 (1994)].

13-10 DISTILLATION

THERMODYNAMIC DATA

INTRODUCTION

Reliable thermodynamic data are essential for the accurate design or analysis of distillation columns. Failure of equipment to perform at specified levels is often attributable, at least in part, to the lack of such data.

This subsection summarizes and presents examples of phase equilibrium data currently available to the designer. The thermodynamic concepts utilized are presented in the subsection "Thermodynamics" of Sec. 4.

PHASE EQUILIBRIUM DATA

For a binary mixture, pressure and temperature fix the equilibrium vapor and liquid compositions. Thus, experimental data are frequently presented in the form of tables of vapor mole fraction y and liquid mole fraction x for one constituent over a range of temperature T for a fixed pressure P or over a range of pressure for a fixed temperature. A compilation of such data, mainly at a pressure of 101.3 kPa (1 atm, 1013 bar), for binary systems (mainly nonideal) is given in Table 13-1. More extensive presentations and bibliographies of such data may be found in Hala, Wichterle, Polak, and Boulik (Vapor-Liquid Equilibrium Data at Normal Pressures, Pergamon, Oxford (1966)), Hala, Oke, and Nagahama (Computer Aided Data Book of Vapor-Liquid Equilibrium, Elsevier, Amsterdam (1975)), Wichterle, Linek, and Hala (Vapor-Liquid Equilibrium Data Bibliography, Elsevier, Amsterdam, 1973, Supplement I, 1976, Supplement II, (1979)), Ge (Vapor-Liquid Equilibrium Data, Elsevier, Amsterdam (1983)), Ge (Vapor-Liquid Equilibrium Data at High Pressure, Elsevier, Amsterdam (1980)), Walas (Phase Equilibria in Chemical Engineering, Butterworth, Boston (1985)), and, particularly, Gmehling and Oken (Vapor-Liquid Equilibrium Data Collection, DECHEMA Chemistry Data Series, vol. 1 (parts 1-10), Frankfurt, 1977).

For application to distillation (a nearly isobaric process), as shown in Figs. 13-5 to 13-15, binary-mixture data are frequently plotted, for a fixed pressure, as y versus x , with a line of 45° slope included for reference, and as T versus y and x . In most binary systems, one of the components is more volatile than the other over the entire composition range. This is the case in Figs. 13-5 and 13-9 for the benzene-toluene system at pressures of both 101.3 and 202.6 kPa (1 and 2 atm), where benzene is more volatile than toluene.

For some binary systems one of the components is more volatile over only a part of the composition range. Two systems of this type, ethyl acetate-ethanol and chloroform-acetone, are shown in Figs. 13-10 to 13-12. Figure 13-10 shows that for two binary systems chloroform is less volatile than acetone below a concentration of 68 mole percent chloroform and that ethyl acetate is less volatile than ethanol below a concentration of 53 mole percent ethyl acetate. Above these concentrations, volatility is reversed. Such mixtures are known as azeotropic mixtures, and the composition in which the reversal occurs, which is the composition in which vapor and liquid compositions are equal, is the azeotropic composition, or azeotrope. The azeotropic liquid may be homogeneous or heterogeneous (two immiscible liquid phases). Many of the binary mixtures of Table 13-1 form homogeneous azeotropes. Non-azeotrope-forming mixtures such as benzene and toluene in Figs. 13-5 and 13-9 can be separated by simple distillation into two essentially pure products. By contrast, simple distillation of azeotropic mixtures will at best yield the azeotrope and one essentially pure species. The distillate and bottoms products obtained depend upon the feed composition and whether a minimum-boiling azeotrope is formed as with the ethyl acetate-ethanol mixture in Fig. 13-11 or a maximum-boiling azeotrope is formed as with the chloroform-acetone mixture in Fig. 13-12. For example, if a mixture of 30 mole percent chloroform and 70 mole percent acetone is fed to a simple distillation column, such as that shown in Fig. 13-1, operating at 101.3 kPa (1 atm), the distillate could approach pure acetone and the bottoms could approach the azeotrope.

An example of heterogeneous azeotrope formation is shown in Fig. 13-13 for the water-normal butanol system at 101.3 kPa. At liquid compositions between 9 and 3 mole percent butanol and between 40 and 100 mole percent butanol, the liquid phase is homogeneous. Phase splitting into two separate liquid phases (one with 3 mole percent butanol and the other with 40 mole percent butanol) occurs for any overall liquid composition between 3 and 40 mole percent butanol. A minimum-boiling heterogeneous azeotrope occurs at 92°C (198°F) when the vapor composition and the overall composition of the two liquid phases are 75 mole percent butanol.

For mixtures containing more than two species, an additional degree of freedom is available for each additional component. Thus, for a four-component system, the equilibrium vapor and liquid compositions are only fixed if the pressure, temperature, and mole fraction of two components are set. Representation of multicomponent vapor-liquid equilibrium data in tabular or graphical form of the type shown earlier for binary systems is either difficult or impossible. Instead, such data, as well as binary-system data, are commonly represented in terms of K values (vapor-liquid equilibrium ratios), which are defined by

$$K_i = y_i/x_i \quad (13-1)$$

and are correlated empirically or theoretically in terms of temperature, pressure, and phase compositions in the form of tables, graphs, and equations. K values are widely used in multicomponent distillation calculations, and the ratio of the K values of two species, called the relative volatility,

$$\alpha_{ij} = K_i/K_j \quad (13-2)$$

is a convenient index of the relative ease or difficulty of separating components i and j by distillation. Rarely is distillation used on a large scale if the relative volatility is less than 1.05, with 1 more volatile than j .

GRAPHICAL K -VALUE CORRELATIONS

As discussed in Sec. 4, the K value of a species is a complex function of temperature, pressure, and equilibrium vapor- and liquid-phase compositions. However, for mixtures of compounds of similar molecular structure and size, the K value depends mainly on temperature and pressure. For example, several major graphical K -value correlations are available for light-hydrocarbon systems. The earliest tables are the DePriester charts [Chem. Eng. Prog. Symp. Ser. 7, 49, 1 (1953)], which cover 12 hydrocarbons (methane, ethylene, ethane, propylene, propane, isobutane, n-butane, isopentane, n-pentane, n-hexane, and n-heptane). These charts are a simplification of the Kellogg charts [Liquid-Vapor Equilibrium in Mixtures of Light Hydrocarbons, MWK Equilibrium Constants, Polyco, Data, (1959)] and include additional experimental data. The Kellogg charts, and hence the DePriester charts, are based primarily on the Benedict-Webb-Rubin equation of state [Chem. Eng. Prog., 47, 419 (1951); 47, 469 (1951)], which can represent both the liquid and the vapor phases and can predict K values quite accurately when the equation constants are available for the components in question.

A trial-and-error procedure is required with any K -value correlation that takes into account the effect of composition. One cannot calculate K values until phase compositions are known, and those cannot be known until the K values are available to calculate them. For K as a function of T and P only, the DePriester charts provide good starting values for the iteration. These nomographs are shown in Fig. 13-14a and b. SI versions of these charts have been developed by Dadybunor [Chem. Eng. Prog., 74(4), 85 (1978)].

The Kellogg and DePriester charts and their subsequent extensions and generalizations use the molar average boiling points of the liquid and vapor phases to represent the composition effect. An alternative measure of composition is the convergence pressure of the system, which is defined as that pressure at which the K values for all the components in an isothermal mixture converge to unity. It is analogous to the critical point for a pure component in the sense that the two

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13-11 THERMODYNAMIC DATA

TABLE 13-1 Constant-Pressure Liquid-Vapor Equilibrium Data for Selected Binary Systems

Component A	Component B	Temperature, °C	Mole Fraction A in		Total pressure, kPa	Reference
			Liquid	Vapor		
Acetone	Chloroform	62.50	0.0517	0.0594	101.3	1
		63.00	0.1000	0.1000		
		63.50	0.1500	0.1500		
		64.00	0.2000	0.2000		
		64.50	0.2500	0.2500		
		65.00	0.3000	0.3000		
		65.50	0.3500	0.3500		
		66.00	0.4000	0.4000		
		66.50	0.4500	0.4500		
		67.00	0.5000	0.5000		
Acetone	Methanol	62.50	0.0517	0.0594	101.3	2
		63.00	0.1000	0.1000		
		63.50	0.1500	0.1500		
		64.00	0.2000	0.2000		
		64.50	0.2500	0.2500		
		65.00	0.3000	0.3000		
		65.50	0.3500	0.3500		
		66.00	0.4000	0.4000		
		66.50	0.4500	0.4500		
		67.00	0.5000	0.5000		
Acetone	Water	62.50	0.0517	0.0594	101.3	3
		63.00	0.1000	0.1000		
		63.50	0.1500	0.1500		
		64.00	0.2000	0.2000		
		64.50	0.2500	0.2500		
		65.00	0.3000	0.3000		
		65.50	0.3500	0.3500		
		66.00	0.4000	0.4000		
		66.50	0.4500	0.4500		
		67.00	0.5000	0.5000		
Carbon tetrachloride	Benzene	62.50	0.0517	0.0594	101.3	4
		63.00	0.1000	0.1000		
		63.50	0.1500	0.1500		
		64.00	0.2000	0.2000		
		64.50	0.2500	0.2500		
		65.00	0.3000	0.3000		
		65.50	0.3500	0.3500		
		66.00	0.4000	0.4000		
		66.50	0.4500	0.4500		
		67.00	0.5000	0.5000		
Chloroform	Methanol	62.50	0.0517	0.0594	101.3	5
		63.00	0.1000	0.1000		
		63.50	0.1500	0.1500		
		64.00	0.2000	0.2000		
		64.50	0.2500	0.2500		
		65.00	0.3000	0.3000		
		65.50	0.3500	0.3500		
		66.00	0.4000	0.4000		
		66.50	0.4500	0.4500		
		67.00	0.5000	0.5000		
Ethanol	Benzene	62.50	0.0517	0.0594	101.3	6
		63.00	0.1000	0.1000		
		63.50	0.1500	0.1500		
		64.00	0.2000	0.2000		
		64.50	0.2500	0.2500		
		65.00	0.3000	0.3000		
		65.50	0.3500	0.3500		
		66.00	0.4000	0.4000		
		66.50	0.4500	0.4500		
		67.00	0.5000	0.5000		

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13-12 DISTILLATION

TABLE 13-1 Constant-Pressure Liquid-Vapor Equilibrium Data for Selected Binary Systems (Continued)

Component A	Component B	Temperature, °C	Mole Fraction A in		Total pressure, kPa	Reference
			Liquid	Vapor		
Ethanol	Water	62.50	0.0517	0.0594	101.3	7
		63.00	0.1000	0.1000		
		63.50	0.1500	0.1500		
		64.00	0.2000	0.2000		
		64.50	0.2500	0.2500		
		65.00	0.3000	0.3000		
		65.50	0.3500	0.3500		
		66.00	0.4000	0.4000		
		66.50	0.4500	0.4500		
		67.00	0.5000	0.5000		
Ethyl acetate	Ethanol	62.50	0.0517	0.0594	101.3	8
		63.00	0.1000	0.1000		
		63.50	0.1500	0.1500		
		64.00	0.2000	0.2000		
		64.50	0.2500	0.2500		
		65.00	0.3000	0.3000		
		65.50	0.3500	0.3500		
		66.00	0.4000	0.4000		
		66.50	0.4500	0.4500		
		67.00	0.5000	0.5000		
Ethylbenzene	Water	62.50	0.0517	0.0594	101.3	9
		63.00	0.1000	0.1000		
		63.50	0.1500	0.1500		
		64.00	0.2000	0.2000		
		64.50	0.2500	0.2500		
		65.00	0.3000	0.3000		
		65.50	0.3500	0.3500		
		66.00	0.4000	0.4000		
		66.50	0.4500	0.4500		
		67.00	0.5000	0.5000		
n-Heptane	Ethanol	62.50	0.0517	0.0594	101.3	10
		63.00	0.1000	0.1000		
		63.50	0.1500	0.1500		
		64.00	0.2000	0.2000		
		64.50	0.2500	0.2500		
		65.00	0.3000	0.3000		
		65.50	0.3500	0.3500		
		66.00	0.4000	0.4000		
		66.50	0.4500	0.4500		
		67.00	0.5000	0.5000		
Methanol	Benzene	62.50	0.0517	0.0594	101.3	11
		63.00	0.1000	0.1000		
		63.50	0.1500	0.1500		
		64.00	0.2000	0.2000		
		64.50	0.2500	0.2500		
		65.00	0.3000	0.3000		
		65.50	0.3500	0.3500		
		66.00	0.4000	0.4000		
		66.50	0.4500	0.4500		
		67.00	0.5000	0.5000		

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12-13

TABLE 12-1 Combustion-Pressure Liquid-Vapor Equilibrium Data for Selected Binary Systems (Continued)

Component A	Component B	Temperature, °C		Mole fraction, A in		Total pressure, kPa	Reference
		Liquid	Vapor	Liquid	Vapor		
Methanol	Ethyl acetate	78.10	69.62	0.0000	0.0000	101.3	12
		78.10	69.62	0.0000	0.0000	101.3	12
		78.10	69.62	0.0000	0.0000	101.3	12
		78.10	69.62	0.0000	0.0000	101.3	12
		78.10	69.62	0.0000	0.0000	101.3	12
		78.10	69.62	0.0000	0.0000	101.3	12
		78.10	69.62	0.0000	0.0000	101.3	12
		78.10	69.62	0.0000	0.0000	101.3	12
		78.10	69.62	0.0000	0.0000	101.3	12
		78.10	69.62	0.0000	0.0000	101.3	12
Methanol	Water	100.0	99.6	0.0000	0.0000	101.3	13
		100.0	99.6	0.0000	0.0000	101.3	13
		100.0	99.6	0.0000	0.0000	101.3	13
		100.0	99.6	0.0000	0.0000	101.3	13
		100.0	99.6	0.0000	0.0000	101.3	13
		100.0	99.6	0.0000	0.0000	101.3	13
		100.0	99.6	0.0000	0.0000	101.3	13
		100.0	99.6	0.0000	0.0000	101.3	13
		100.0	99.6	0.0000	0.0000	101.3	13
		100.0	99.6	0.0000	0.0000	101.3	13
Methyl acetate	Methanol	57.00	57.00	0.0000	0.0000	101.3	14
		57.00	57.00	0.0000	0.0000	101.3	14
		57.00	57.00	0.0000	0.0000	101.3	14
		57.00	57.00	0.0000	0.0000	101.3	14
		57.00	57.00	0.0000	0.0000	101.3	14
		57.00	57.00	0.0000	0.0000	101.3	14
		57.00	57.00	0.0000	0.0000	101.3	14
		57.00	57.00	0.0000	0.0000	101.3	14
		57.00	57.00	0.0000	0.0000	101.3	14
		57.00	57.00	0.0000	0.0000	101.3	14
1-Propanol	Water	100.0	99.6	0.0000	0.0000	101.3	15
		100.0	99.6	0.0000	0.0000	101.3	15
		100.0	99.6	0.0000	0.0000	101.3	15
		100.0	99.6	0.0000	0.0000	101.3	15
		100.0	99.6	0.0000	0.0000	101.3	15
		100.0	99.6	0.0000	0.0000	101.3	15
		100.0	99.6	0.0000	0.0000	101.3	15
		100.0	99.6	0.0000	0.0000	101.3	15
		100.0	99.6	0.0000	0.0000	101.3	15
		100.0	99.6	0.0000	0.0000	101.3	15
2-Propanol	Water	100.0	99.6	0.0000	0.0000	101.3	16
		100.0	99.6	0.0000	0.0000	101.3	16
		100.0	99.6	0.0000	0.0000	101.3	16
		100.0	99.6	0.0000	0.0000	101.3	16
		100.0	99.6	0.0000	0.0000	101.3	16
		100.0	99.6	0.0000	0.0000	101.3	16
		100.0	99.6	0.0000	0.0000	101.3	16
		100.0	99.6	0.0000	0.0000	101.3	16
		100.0	99.6	0.0000	0.0000	101.3	16
		100.0	99.6	0.0000	0.0000	101.3	16

12-14

TABLE 12-1 Combustion-Pressure Liquid-Vapor Equilibrium Data for Selected Binary Systems (Continued)

Component A	Component B	Temperature, °C		Mole fraction, A in		Total pressure, kPa	Reference
		Liquid	Vapor	Liquid	Vapor		
Tetrahydrofuran	Water	22.00	22.00	0.0000	0.0000	101.3	17
		22.00	22.00	0.0000	0.0000	101.3	17
		22.00	22.00	0.0000	0.0000	101.3	17
		22.00	22.00	0.0000	0.0000	101.3	17
		22.00	22.00	0.0000	0.0000	101.3	17
		22.00	22.00	0.0000	0.0000	101.3	17
		22.00	22.00	0.0000	0.0000	101.3	17
		22.00	22.00	0.0000	0.0000	101.3	17
		22.00	22.00	0.0000	0.0000	101.3	17
		22.00	22.00	0.0000	0.0000	101.3	17
Water	Acetic acid	100.0	100.0	0.0000	0.0000	101.3	18
		100.0	100.0	0.0000	0.0000	101.3	18
		100.0	100.0	0.0000	0.0000	101.3	18
		100.0	100.0	0.0000	0.0000	101.3	18
		100.0	100.0	0.0000	0.0000	101.3	18
		100.0	100.0	0.0000	0.0000	101.3	18
		100.0	100.0	0.0000	0.0000	101.3	18
		100.0	100.0	0.0000	0.0000	101.3	18
		100.0	100.0	0.0000	0.0000	101.3	18
		100.0	100.0	0.0000	0.0000	101.3	18
Water	2-Propanol	100.0	100.0	0.0000	0.0000	101.3	19
		100.0	100.0	0.0000	0.0000	101.3	19
		100.0	100.0	0.0000	0.0000	101.3	19
		100.0	100.0	0.0000	0.0000	101.3	19
		100.0	100.0	0.0000	0.0000	101.3	19
		100.0	100.0	0.0000	0.0000	101.3	19
		100.0	100.0	0.0000	0.0000	101.3	19
		100.0	100.0	0.0000	0.0000	101.3	19
		100.0	100.0	0.0000	0.0000	101.3	19
		100.0	100.0	0.0000	0.0000	101.3	19
Water	Formic acid	100.0	100.0	0.0000	0.0000	101.3	20
		100.0	100.0	0.0000	0.0000	101.3	20
		100.0	100.0	0.0000	0.0000	101.3	20
		100.0	100.0	0.0000	0.0000	101.3	20
		100.0	100.0	0.0000	0.0000	101.3	20
		100.0	100.0	0.0000	0.0000	101.3	20
		100.0	100.0	0.0000	0.0000	101.3	20
		100.0	100.0	0.0000	0.0000	101.3	20
		100.0	100.0	0.0000	0.0000	101.3	20
		100.0	100.0	0.0000	0.0000	101.3	20
Water	Glycol	100.0	100.0	0.0000	0.0000	101.3	21
		100.0	100.0	0.0000	0.0000	101.3	21
		100.0	100.0	0.0000	0.0000	101.3	21
		100.0	100.0	0.0000	0.0000	101.3	21
		100.0	100.0	0.0000	0.0000	101.3	21
		100.0	100.0	0.0000	0.0000	101.3	21
		100.0	100.0	0.0000	0.0000	101.3	21
		100.0	100.0	0.0000	0.0000	101.3	21
		100.0	100.0	0.0000	0.0000	101.3	21
		100.0	100.0	0.0000	0.0000	101.3	21

THERMODYNAMIC DATA 13-15

TABLE 13-1 Constant-Pressure Liquid-Vapor Equilibrium Data for Selected Binary Systems (Continued)

Component A	Component B	Temperature, °C	Mole fraction x in		Total pressure, kPa	Reference
			Liquid	Vapor		
		175.2	0.1756	0.9989		
		181.5	0.3094	0.9964		
		187.2	0.3947	0.9978		
		195.5	0.4685	0.9978		
		211.5	0.6332	0.9975		
		212.9	0.7059	0.9983		
		213.2	0.7385	0.9984		
		205.3	0.8410	0.9986		
		209.0	1.0000	1.0000		

NOTE: To convert degrees Celsius to degrees Fahrenheit, $^{\circ}\text{C} \times 1.8 + 32 = ^{\circ}\text{F}$. To convert kilopascals to pounds force per square inch, multiply by 0.145.Koyu, Kato, Sano, and Hiden, *Kogyo Kagaku Zasshi*, 38, 537 (1965).Mannick and Sauer, *AIChE J.*, 38, 578 (1965).Kojima, Tochig, Seki, and Watanabe, *Kogyo Kagaku Zasshi*, 38, 149 (1965).

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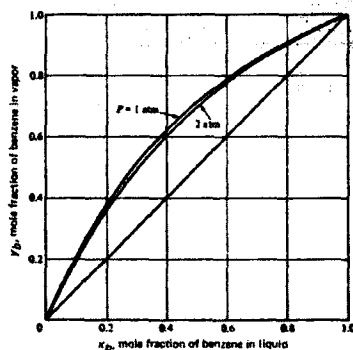
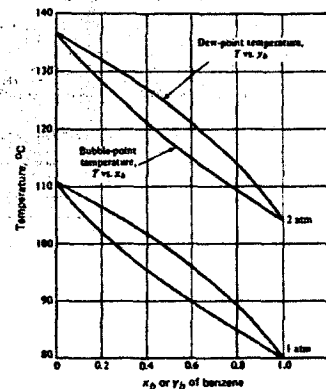
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FIG. 13-9 Isobaric vapor-liquid equilibrium data for benzene-toluene (Brown, Sealed Canisters in Chemical Processing, Prentice-Hall, Englewood Cliffs, NJ, 1972).

13-16 DISTILLATION

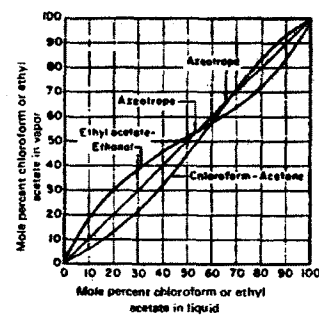


FIG. 13-10 Vapor-liquid equilibrium curves for the ethyl acetate-ethanol and chloroform-acetone systems at 101.3 kPa (1 atm).

phases become indistinguishable. The behavior of a complex mixture of hydrocarbons for a convergence pressure of 34.5 MPa (5000 psia) is illustrated in Fig. 13-15.

Two major graphical correlations based on convergence pressure as the third parameter (besides temperature and pressure) are the charts published by the Chemical Processors Association (CPA, Engineering Data Book, 9th ed., Tulsa, 1981) and the charts of the American Petroleum Institute (API, Technical Data Book—Petroleum Refining, New York, 1969) based on the procedures from Hadden and Grayson (Hydrocarbon Process., Pet. Refiner, 40(9), 207 (1961)). The former uses the method proposed by Hadden (Chem. Eng. Prog. Symp. Ser. 7, 49, 53 (1953)) for the prediction of convergence pressure as a function of composition. The basis for Hadden's method is illustrated in Fig. 13-16, where it is shown that the critical loci for various mixtures of methane-propane-pentane fall within the area circumscribed by the three binary loci. (This behavior is not always typical of more nonideal systems.) The critical loci for the ternary mixtures vary linearly, at constant temperature, with weight percent propane on a methane-free basis. The essential point is that critical loci for mixtures are independent of the concentration of the lightest component in a mixture. This permits representation of a multicomponent mixture as a pseudo binary. The light component in this pseudo binary is the lightest species present (to a reasonable extent) in the multicomponent mixture. The heavy component is a pseudo substance whose critical temperature is an average of all other components in the multicomponent

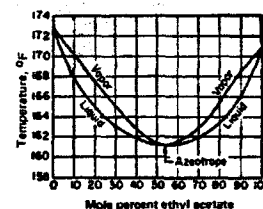


FIG. 13-11 Liquid boiling points and vapor condensation temperatures for minimum-boiling azeotropic mixtures of ethyl acetate and ethanol at 101.3 kPa (1 atm) total pressure.

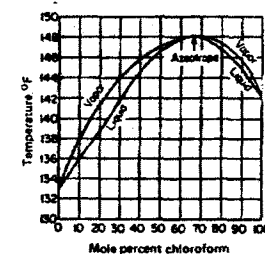


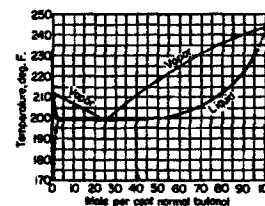
FIG. 13-12 Liquid boiling points and vapor condensation temperatures for maximum-boiling azeotropic mixtures of chloroform and acetone at 101.3 kPa (1 atm) total pressure.

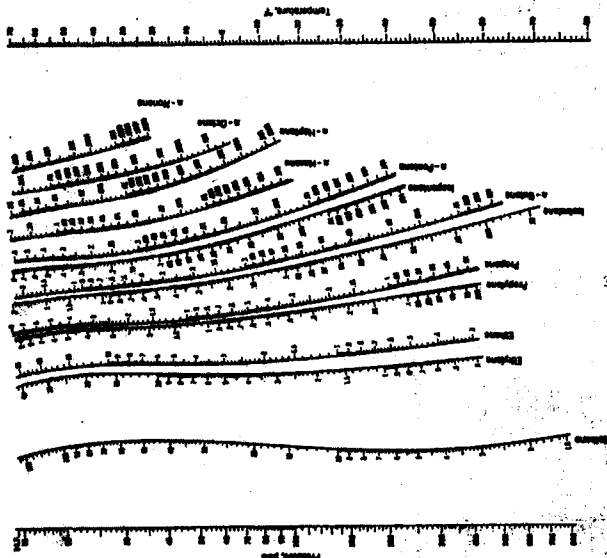
mixture. This pseudocritical point can then be located on a P - T diagram consisting of the critical points for all compounds covered by the charts, and a critical locus can be drawn for the pseudo binary by interpolation between various real binary curves. Convergence pressure for the mixture at the desired temperature is read from the assumed loci at the desired system temperature. This method is illustrated in the left half of Fig. 13-17 for the methane-propane-pentane ternary. Associated K values for pentane at 104°C (220°F) are shown to the right as a function of mixture composition (for convergence pressure).

The CPA convergence-pressure charts are primarily for alkane and alkene systems but do include charts for nitrogen, carbon dioxide, and hydrogen sulfide. The charts may not be valid when appreciable amounts of naphthenes or aromatics are present; the API charts use special procedures for such cases. Useful extensions of the convergence-pressure concept to more varied mixtures include the nomographs of Winn (Chem. Eng. Prog. Symp. Ser. 2, 46, 131 (1953)), Hadden and Grayson (op. cit.), and Calander, Hipkin, and Lenoir (J. Chem. Eng. Data, 5, 251 (1960)).

ANALYTICAL K -VALUE CORRELATIONS

The widespread availability and utilization of digital computers for distillation calculations have given impetus to the development of analytical expressions for K values. McWilliams (Chem. Eng., 80(25), 138 (1973)) presents a regression equation and accompanying regression coefficients that represent the DePriester charts of Fig. 13-14. Regression equations and coefficients for various versions of the CPA convergence-pressure charts are available from the CPA.

FIG. 13-13 Vapor-liquid equilibrium data for the n -butanol-water system at 101.3 kPa (1 atm); phase splitting and heterogeneous azeotropic formation.



1959, 2314. K values ($K = \rho/\eta$) in light-hydrocarbon systems. (a) Low-temperature range [DeFries, Chem. Eng. Prog. Symp. Ser. 7, 49, 1 (1953)]

Preferred analytical correlations are less empirical in nature and most often are theoretically based on one of two exact thermodynamic formulations, as derived in Sec. 4. When a single pressure-volume-temperature (PVT) equation of state is applicable to both vapor and liquid phases, the formulation used is

(133)

[illegible]

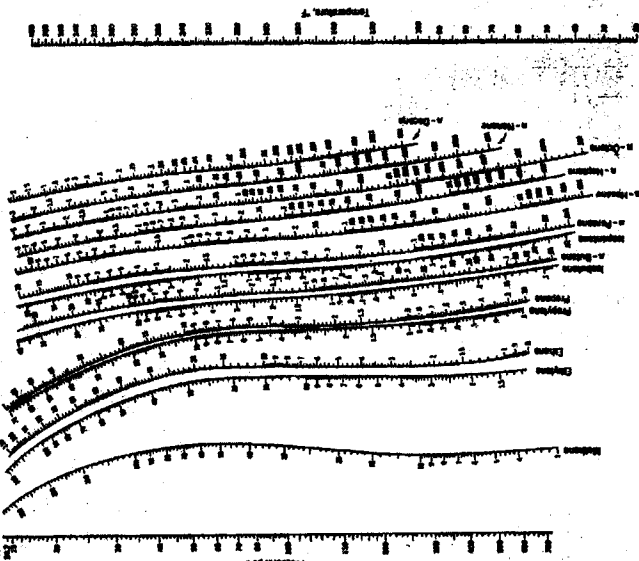
variables, including the pressure region. Computer programs for K values were developed from the SRK P and T correlations of time are widely available in all computerized process design and simulation programs. The ability of the SRK correlation to predict K values over a wide range of pressures and temperatures is shown in Figure 1. However, the pressure approaches the convergence pressure is shown for multicomponent systems in Fig. 12-18. Similar results are achieved with the PR correlation. The Wong-Sandler mixing rules for cubic equations of state give somewhat better results for the extended to mixtures of organic chemicals¹⁴ than the SRK mixing rules.¹⁵

Others and Sandler^{16,17} also present a reformulated version by

$$K = \gamma^{\mu} \phi_{\mu}^{\nu} / \phi^{\nu}$$

where different equations of state may be used to predict the pure-component liquid fugacity coefficients ϕ_i^L and the vapor-liquid fugacity coefficient, and any one of a number of mixture free-energy models may be used to obtain the liquid activity coefficients γ_i^L . At low to moderate pressures, accurate prediction of the latter is crucial to the combination of Eq. (13a).

When either Eq. (13-3) or Eq. (13-4) can be applied, the former is generally preferred because it involves only a single equation of state



20. 13-16 (Continued) K values ($K = \eta/\eta_0$) in light-hydrocarbon systems. (c) High-temperature range. (Defensive Chem. Eng. Prog. Ser. No. 7, 49, 1 (1953))

applicable to both phases and thus would seem to offer greater consistency. In addition, the quantity Φ^* in Eq. (13-4) is hypothetical for any components that are supercritical. In that case, a modification of Eq. (12-4) that uses Henry's law is sometimes applied.

[illegible]

the CS correlation to higher temperatures and pressures and give improved predictions for hydrogen [in Greenkorn, and Chao and Altschuler, 41, 1942 (1985)] present a revised correlation for the standard-state liquid fugacity of hydrogen, applicable from 200 to 730 K.

For mixtures containing polar substances, more complex procedures are required for γ^E that involve binary-interaction parameters for the various components. The γ^E values for the various components of each pair of components in the mixture are required for use in Eqs. [13-34], as discussed in Sec. 4. Some popular equations for the γ^E values are those of Wilson, NRTL, UNIQUAC, and UNIQAC equations. Extensive lists of binary-interaction parameters for all the components of the various mixtures are given by Gmehling and Neundorfer [13-35]. The UNIQUAC equations are given by Gmehling and Praeger [13-36]. They obtained the parameters for their systems from 1913 to 1960. From the list of their experimental data, they selected the data that were most reliable and used these data to determine the parameters. They used the experimental data to determine the parameters for the various systems. The parameters for the various systems are given by Gmehling and Praeger [13-36]. The parameters for the various systems are given by Gmehling and Praeger [13-36].

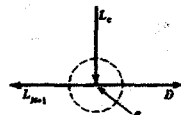


FIG. 13-21 Stream divider.

reflux L_{n+1} . The divider is permitted to operate nonadiabatically if desired. Three mass streams and one possible "energy stream" are involved, so

$$N^* = 3(C + 2) + 1 = 3C + 7$$

Each mass stream contributes $C + 2$ variables, but an energy stream has only its rate q as a variable. The independent restrictions are as follows:

	N^*
Inherent	
T and P densities between L_{n+1} and D	2
Concentration identities between L_{n+1} and D	$C - 1$
Mass balance	C
Energy balance	$2C - 5$

The number of design variables for the element is given by

$$N^* = N^* - N^* = (3C + 7) - (3C + 2) = C + 5$$

Specification of the feed stream L_{n+1} ($C + 2$ variables), the ratio L_{n+1}/D , the "heat leak" q , and the pressure of either stream leaving the divider utilizes these design variables and defines one unique operation of the divider.

A simple equilibrium stage (no feed or distillate) is depicted in Fig. 13-22. Four mass streams and a heat-leak (or heat-addition) stream provide the following number of variables:

$$N^* = 4(C + 3) + 1 = 4C + 9$$

Vapor and liquid streams V_n and L_{n+1} , respectively are in equilibrium with each other by definition and therefore are at the same T and P. These two inherent identities when added to C-component balances, one energy balance, and the C phase-distribution relationships give

$$N^* = 3C + 3$$

Then

$$N^* = N^* - N^* = (4C + 9) - (3C + 3) = C + 6$$

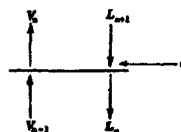


FIG. 13-22 Simple equilibrium stage.

DEGREES OF FREEDOM AND DESIGN VARIABLES 13-23

These design variables can be utilized as follows:

Specification	N^*
Specification of L_{n+1} stream	$C + 2$
Specification of V_n stream	$C + 2$
Pressure of either leaving stream	1
Heat leak q	1
	$2C + 6$

The results of the analyses for all the various elements commonly encountered in distillation processes are summarized in Table 13-5. Details of the analyses are given by Smith (*Design of Equilibrium Stage Processes*, McGraw-Hill, New York, 1967) and in a somewhat different form by Henley and Seader (op. cit.).

ANALYSIS OF UNITS

A "unit" is defined as a combination of elements and may or may not constitute the entire process. By definition

$$N^* = N^* - \sum N^*$$

and

$$N^* = N^* - N^*$$

where N^* refers to new restricting relationships (densities) that may arise when elements are combined. N^* does not include any of the restrictions considered in calculating the N^* 's for the various elements. It includes only the stream identities that exist in each interstream between two elements. The stream variables ($C - 2$) were counted in each of the two elements when their respective N^* 's were calculated. Therefore, ($C + 2$) new restricting relationships must be counted for each interstream in the combination of elements to prevent redundancy.

The simple absorber column shown in Fig. 13-23 will be analyzed here to illustrate the procedure. This unit consists of a series of simple equilibrium stages of the type in Fig. 13-22. Specification of the number of stages N utilizes the single repetition variable and

$$N^* = N^* - \sum N^* = 1 + N(2C + 6)$$

since in Table 13-5 $N^* = 2C + 6$ for a simple equilibrium stage. There are $2(N - 1)$ interstreams, and therefore $2(N - 1)(C + 2)$ new identities (see previously counted) come into existence when elements are combined. Subtraction of these restrictions from N^* gives N^* , the design variables that must be specified.

$$\begin{aligned} N^* &= N^* - N^* = N^* - \sum N^* \\ &= [1 + N(2C + 6)] - [2(N - 1)(C + 2)] \\ &= 2C + 2N + 5 \end{aligned}$$

TABLE 13-5 Design Variables N^* for Various Elements

Element	N^*	N^*	N^*
Homogeneous stream	$C + 2$	0	$C + 2$
Stream divider	$3C + 7$	$2C + 2$	$C + 5$
Stream mixer	$3C + 7$	$C + 1$	$2C + 6$
Pump	$2C + 5$	$C + 1$	$C + 4$
Heater	$2C + 5$	$C + 1$	$C + 4$
Cooler	$2C + 5$	$C + 1$	$C + 4$
Total condenser	$2C + 5$	$C + 1$	$C + 4$
Total reboiler	$2C + 5$	$C + 1$	$C + 4$
Partial condenser	$3C + 7$	$2C + 3$	$C + 4$
Partial reboiler	$3C + 7$	$2C + 3$	$C + 4$
Simple equilibrium stage	$4C + 9$	$3C + 3$	$2C + 6$
Feed stage	$5C + 11$	$3C + 3$	$3C + 8$
Substream stage	$5C + 11$	$3C + 4$	$3C + 7$
Adiabatic equilibrium flash	$3C + 6$	$2C + 3$	$C + 3$
Nonadiabatic equilibrium flash	$3C + 7$	$3C + 3$	$C + 4$

13-24 DISTILLATION

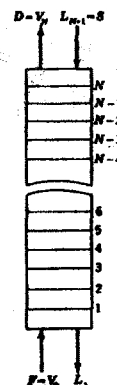


FIG. 13-23 Simple absorber.

These might be used as follows:

Specifications	N^*
Two feed streams	$2C + 4$
Number of stages N	1
Pressure of either stream leaving each stage	N
Heat leak for each stage	N
	$2C + 2N + 5$

A more complex unit is shown in Fig. 13-24, which is a schematic diagram of a distillation column with one feed, a total condenser, and a partial reboiler. Dashed lines encircle the six connected elements (or units) that constitute the distillation operation. The variables N^* that must be considered in the analysis of the entire process are just the sum of the N^* 's for these six elements since here $N^* = 0$. Using Table 13-5,

Element (or unit)	N^*	N^*	N^*
Total condenser	C	+4	
Reflux divider	C	+5	
$N - (M + 1)$ equilibrium stages	$2C + 2(N - M - 1)$	+5	
Feed stage	3C	+8	
$(M - 1)$ equilibrium stages	$3C + 2(M - 1)$	+5	
Partial reboiler	C	+4	
	$10C + 2N$	+27	

Here, the two units of $N - (M + 1)$ and $(M - 1)$ stages are treated just like elements. Nine interstreams are created by the combination of elements, so

$$N^* = 9(C + 2) = 9C + 18$$

The number of design variables is

$$N^* = C - 2N + 9N^* - N^* = (10C + 2N + 27) - (9C + 18)$$

One set of specifications that is particularly convenient for computer solutions is:

Specifications	N^*
Pressure of either stream leaving each stage (including reboiler)	N
Pressure of stream leaving condenser	1
Pressure of either stream leaving reflux divider	N - 1
Heat leak for each stage (including reboiler)	N
Heat leak for reflux divider	1
Feed stream	C + 2
Reflux temperature	1
Total number of stages N	1
Number of stages below feed M	1
Distillate rate D/F	1
Reflux rate (L_{n+1}/D)	1
	$C + 2N + 9$

Other specifications often used in place of one or more of the last four listed are the fractional recovery of one component in either D or B and/or the concentration of one component in either D or B.

OTHER UNITS AND COMPLEX PROCESSES

In Table 13-6, the number of design variables is summarized for several distillation-type separation operations, most of which are shown in Fig. 13-7. For columns not shown in Figs. 13-1 or 13-7 that

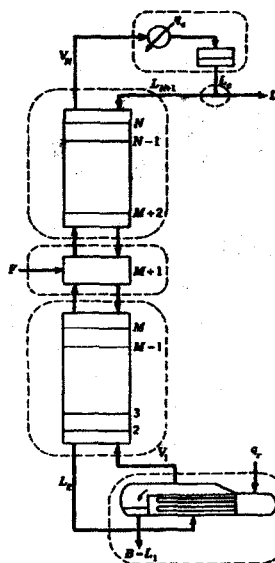


FIG. 13-24 Distillation column with one feed, a total condenser, and a partial reboiler.

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SINGLE-STAGE EQUILIBRIUM-FLASH CALCULATIONS 13-25

involve additional feeds and/or sidestreams, add $(C + 3)$ degrees of freedom for each additional feed ($C + 2$ to define the feed and 1 to designate the feed stage) and 2 degrees of freedom for each sidestream (1 for the sidestream flow rate and 1 to designate the sidestream stage location). Any number of elements of C.V.s can be combined to form complex processes. No new rules beyond those developed earlier are necessary for their analysis. When applied to the thermally coupled distillation process of Fig. 13-6b, the result is $N^* = 2(N + M) + C + 15$. Further examples are given in Henley and Seader (op. cit.). An alternative method for determining the degrees of freedom for equipment and processes is given by Floudas, *Chem. Eng. Sci.*, **49**, 2507 (1994).

TABLE 13-6 Design Variables N^* for Separation Units

Unit	N^*
Distillation (partial vaporizer-total condenser)	$C + 2N + 9$
Distillation (partial reboiler-partial condenser)	$C + 2N + 8$
Absorption	$2C + 2N + 5$
Reabsorption (partial condenser)	$C + 2N + 1$
Stripping	$2C + 2N + 5$
Reboiled stripping (partial reboiler)	$C + 2N + 3$
Reboiled absorption (partial reboiler)	$2C + 2N + 5$
Reboiled stripping (total condenser)	$2C + 2N + 9$
Stripped distillation (partial reboiler-total condenser)	$2C + 2N + 12$

* N includes reboiler, but not condenser

SINGLE-STAGE EQUILIBRIUM-FLASH CALCULATIONS

INTRODUCTION

The simplest continuous-distillation process is the adiabatic single-stage equilibrium-flash process, pictured in Fig. 13-25. Feed temperature and the pressure drop across the valve are adjusted to vaporize the feed to the desired extent, while the drum provides disengaging space to allow the vapor to separate from the liquid. The expansion across the valve is at constant enthalpy, and this fact can be used to calculate T_2 (or T_1) to give a desired V/L .

From Table 13-6 it can be seen that the variables subject to the designer's control are $C + 3$ in number. The most common way to utilize these is to specify the feed rate, composition, and pressure ($C + 1$ variables) plus the drum temperature T_2 and pressure P_2 . This operation will give one point on the equilibrium-flash curve shown in Fig. 13-26. This curve shows the relation at constant pressure between the fraction V/F of the feed flashed and the drum temperature. The temperature at $V/F = 0.0$ when the first bubble of vapor is about to form (saturated liquid) is the bubble-point temperature of the feed mixture, and the value at $V/F = 1.0$ when the first droplet of liquid is about to form (saturated vapor) is the dew-point temperature.

BUBBLE POINT AND DEW POINT

For a given drum pressure and feed composition, the bubble- and dew-point temperatures bracket the temperature range of the equilibrium flash. At the bubble-point temperature, the total vapor pressure exerted by the mixture becomes equal to the confining drum pressure, and it follows that $\sum y_i = 1.0$ as the bubble formed. Since $y_i = K_i x_i$, and since the x_i will equal the feed concentrations (determined by z_i), calculation of the bubble-point temperature involves a trial-and-error search for the temperature which, at the specified pressure, makes $\sum K_i x_i = 1.0$. If instead the temperature is specified, one can find the bubble-point pressure that satisfies this relationship:

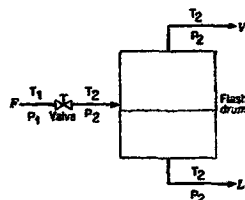


FIG. 13-25 Equilibrium-flash separator

At the dew-point temperature y_i still equals x_i , and the relationship $\sum x_i = \sum z_i/K_i = 1.0$ must be satisfied. As in the case of the bubble point, a trial-and-error search for the dew-point temperature at a specified pressure is involved. Or, if the temperature is specified, the dew-point pressure can be calculated.

ISOTHERMAL FLASH

The calculation for a point on the flash curve that is intermediate between the bubble point and the dew point is referred to as an isothermal-flash calculation because T_2 is specified. Except for an ideal binary mixture, procedures for calculating an isothermal flash are iterative. A popular method is the following, due to Rachford and Rice [J. *Fuel Technol.*, **4**(10), sec. 1, p. 19, and sec. 2, p. 3 (October 1952)]. The component mole balance ($Fz_i = Vy_i + Lx_i$), phase-distribution relation ($K_i = y_i/x_i$), and total mole balance ($F = V + L$) can be combined to give

$$x_i = \frac{z_i}{1 + \frac{V}{F}(K_i - 1)} \quad (13-12)$$

$$y_i = \frac{K_i z_i}{1 + \frac{V}{F}(K_i - 1)} \quad (13-13)$$

$$\text{Since } \sum x_i = \sum y_i = 0,$$

$$f(V) = \sum \frac{z_i(1 - K_i)}{1 + \frac{V}{F}(K_i - 1)} = 0 \quad (13-14)$$

Equation (13-14) is solved iteratively for V/F , followed by the calculation of values of x_i and y_i from Eqs. (13-12) and (13-13) and L from the total mole balance. Any one of a number of numerical root-finding

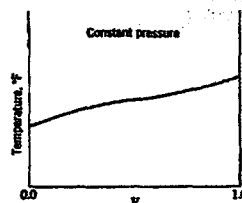


FIG. 13-26 Equilibrium-flash curve

13-26 DISTILLATION

procedures such as the Newton-Raphson, secant, false-position, or bisection method can be used to solve Eq. (13-14). Values of K_i are constants if they are independent of liquid and vapor compositions. Then the resulting calculations are straightforward. Otherwise, the K_i values must be periodically updated for composition effects, perhaps after each iteration, using guessed values of x_i and y_i from Eqs. (13-12) and (13-13). Generally, the iterations are continued until the calculated value of V/F differs by no more than ± 0.0005 the value of V/F that was used to initiate that iteration. When converged, $\sum x_i$ and $\sum y_i$ will each be very close to a value of 1, and, if desired, T_2 can be computed from an energy balance around the valve if no heat exchanger is used. Alternatively, T_2 is fixed as mentioned earlier; a heat exchanger must be added before, after, or in place of the valve with the required heat duty being calculated from an energy balance. The limits of applicability of Eqs. (13-12) to (13-14) are the bubble point, at which $V = 0$ and $x_i = z_i$, and the dew point, at which $L = 0$ and $y_i = z_i$, at which Eq. (13-2) reduces to the bubble-point equation

$$\sum K_i z_i = 1 \quad (13-15)$$

and the dew-point equation

$$\sum \frac{z_i}{K_i} = 1 \quad (13-16)$$

For a binary feed, specification of the flash-drum temperature and pressure fixes the equilibrium-phase concentrations, which are related to the K values by

$$x_1 = (1 - K_2)/(K_1 - K_2) \quad \text{and} \quad y_1 = (K_1 z_2 - K_2)/(K_1 - K_2)$$

The mole balance can be rearranged to

$$\frac{V}{F} = \frac{z_1(K_1 - K_2) + (1 - K_2) - 1.0}{K_1 - 1.0}$$

If K_1 and K_2 are functions of temperature and pressure only (ideal solutions), the flash curve can be calculated directly without iteration.

ADIABATIC FLASH

In Fig. 13-25, if P_2 and the feed-stream conditions (i.e., F, z_i, T_1, P_1) are known, then the calculation of T_2, V, L, y_i , and x_i is referred to as an adiabatic flash. In addition to Eqs. (13-12) to (13-14) and the total mole balance, the following energy balance around both the valve and the flash drum combined must be included:

$$H^*F = H^*V + H^*L \quad (13-17)$$

Taking a basis of $F = 1.0$ mol and eliminating L with the total mole balance, Eq. (13-17) becomes

$$f(V, T_2) = H^* - V(H^* - H^*) - H^* = 0 \quad (13-18)$$

With T_2 now unknown, Eq. (13-17) becomes

$$f_1(V, T_2) = \sum \frac{z_i(1 - K_i)}{1 + V/(K_i - 1)} = 0 \quad (13-19)$$

A number of iterative procedures have been developed for solving Eqs. (13-18) and (13-19) simultaneously for V and T_2 . Frequently, and especially if the feed contains components of a narrow range of volatility, convergence is rapid for a tearing method in which a value of T_2 is

assumed, Eq. (13-19) is solved iteratively by the isothermal-flash procedure, and, using that value of V , Eq. (13-18) is solved iteratively for a new approximation of T_2 , which is then used to initiate the next cycle until T_2 and V converge. However, if the feed contains components of a wide range of volatility, it may be best to invert the sequence and assume a value for V , solve Eq. (13-19) for T_2 , solve Eq. (13-18) for V , and then repeat the cycle. If K values and/or enthalpies are sensitive to the unknown phase compositions, it may be necessary simultaneously to solve Eqs. (13-18) and (13-19) by a Newton or other suitable derivative technique. Alternatively, the two-tier method of Boston and Britt [*Comput. Chem. Eng.*, **3**, 109 (1978)], which is also suitable for difficult isothermal-flash calculations, may be applied.

OTHER FLASH SPECIFICATIONS

Flash-drum specifications in addition to (P_2, T_2) and $(F, \text{adiabatic})$ are also possible but must be applied with care, as discussed by Michelhen [*Comp. Chem. Engng.*, **17**, 431 (1993)]. Most computer-aided process design and simulation programs permit a wide variety of flash specifications.

THREE-PHASE FLASH

Single-stage equilibrium-flash calculations become considerably more complex when an additional liquid phase can form, as from mixtures of water with hydrocarbons. Procedures for computing such situations are referred to as three-phase flash methods, which are given for the general case by Henley and Rosen (*Material and Energy Balance Computations*, Wiley, New York, 1969, chap. 8). When the two liquid phases are almost mutually insoluble, they can be considered separately and relatively simple procedures apply as discussed by Smith (*Design of Equilibrium Stage Processes*, McGraw-Hill, New York, 1983). Condensation of such mixtures may result in one liquid phase being formed before the other. Computer-aided process design and simulation programs all contain a Gibbs free-energy routine that can compute a three-phase flash by minimization of Gibbs free energy. Many difficult aspects of flash calculations are discussed by Michelhen [*Fluid Phase Equil.*, **9**, 1, 21 (1992)].

COMPLEX MIXTURES

Feed analyses in terms of component concentrations are usually not available for complex hydrocarbon mixtures with a final normal boiling point above about 38°C (100°F) (*n*-pentane). One method of handling such a feed is to break it down into pseudo components (pseudo-boiling fractions) and then estimate the mole fraction and K value for each such component. Edmister [*Ind. Eng. Chem.*, **47**, 1693 (1955)] and Marcell (*Data Book on Hydrocarbons*, Van Nostrand, Princeton, N.J., 1958) gave charts that are useful for this estimation. Once K values are available, the calculation proceeds as described above for multicomponent mixtures. Another approach to complex mixtures is to obtain an American Society for Testing and Materials (ASTM) or true-boiling point (TBP) curve for the mixture and then use empirical correlations to construct the atmospheric-pressure equilibrium-flash curve (EFV), which can then be corrected to the desired operating pressure. A discussion of this method and the necessary charts are presented in a later subsection entitled "Petroleum and Complex-Mixture Distillation."

GRAPHICAL METHODS FOR BINARY DISTILLATION

INTRODUCTION

Multistage distillation under continuous, steady-state operating conditions is widely used in practice to separate a variety of mixtures. Table 13-7, taken from the study of M. Dweck, Wenzburg, and Armstrong [*Am. Inst. Chem. Eng. J. Symp. Ser.* **76**, 192, 10 (1980)] lists key components for 27 industrial distillation processes. The design of multiequilibrium-stage columns can be accomplished by graphical techniques when the feed mixture contains only two components. The x - y diagram

[McCabe and Thiele, *Ind. Eng. Chem.*, **17**, 605 (1925)] utilizes only equilibrium and mole-balance relationships but approximates representations only for those systems in which energy effects on vapor and liquid rates leaving the stages are negligible. The enthalpy-concentration diagram [Ponchon, *Chem. Mod.*, **13**, 20, 55 (1921); and Savarit, *Ind. Metiers*, **63**, 142, 178, 241, 266, 307 (1922)] utilizes the energy balance also and is rigorous when enough calorimetric data are available to construct the diagram without assumptions.

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OPERACIONES DE TRANSFERENCIA DE MASA

ROBERT E. TREYBAL

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ABSORCIÓN DE GASES

La absorción de gases es una operación en la cual una mezcla gaseosa se pone en contacto con un líquido, a fin de disolver de manera selectiva uno o más componentes del gas y de obtener una solución de éstos en el líquido. Por ejemplo, el gas obtenido como subproducto en los hornos de coque, se lava con agua para eliminar el amoníaco; después se lava con un aceite para eliminar los vapores de benceno y de tolueno. Para que el molesto sulfuro de hidrógeno sea eliminado de un gas de este tipo o de hidrocarburos gaseosos naturales, el gas o los hidrocarburos se lavan con diferentes soluciones alcalinas que absorben a dicho sulfuro. Los valiosos vapores de un disolvente, acarreados por una corriente gaseosa pueden recuperarse y luego ser reutilizados; basta lavar el gas con un disolvente adecuado a los vapores. Estas operaciones requieren la transferencia de masa de una sustancia en la corriente gaseosa al líquido. Cuando la transferencia de masa sucede en la dirección opuesta, es decir, del líquido al gas, la operación se conoce como desorción. Por ejemplo, el benceno y el tolueno se eliminan del aceite que se mencionó antes poniendo en contacto la solución líquida con vapor, de tal forma que los vapores entran en la corriente gaseosa y son arrastrados; en consecuencia, el aceite de absorción puede utilizarse nuevamente. Los principios de la absorción y la desorción son básicamente los mismos, así que las dos operaciones pueden estudiarse al mismo tiempo.

Generalmente, estas operaciones sólo se utilizan para la recuperación o eliminación del soluto. Una buena separación de solutos entre sí, exige técnicas de destilación fraccionada.

DESTILACIÓN

La destilación es un método para separar los componentes de una solución; depende de la distribución de las sustancias entre una fase gaseosa y una líquida, y se aplica a los casos en que todos los componentes **están** presentes en las dos fases. En vez de introducir una nueva sustancia en la mezcla, con el fin de obtener la segunda fase (como se hace en la absorción o **desorción** de gases) la nueva fase se crea por evaporación o **condensación** a partir de la solución original.

Con objeto de aclarar la diferencia entre la destilación y las otras operaciones, se va a citar algunos ejemplos específicos. Cuando se separa una solución de sal común en agua, el agua puede evaporarse completamente de la solución sin eliminar la sal, puesto que esta última, para todos los fines prácticos, casi no es volátil en las condiciones predominantes. Esta es la operación de evaporación. Por otra parte, la **destilación** se refiere a separar soluciones en que todos los componentes son apreciablemente volátiles. A esta categoría corresponde la separación de los componentes de una solución líquida, de amoníaco y agua. Si la solución de amoníaco en agua se pone en contacto con aire, el cual es básicamente insoluble en el líquido, el amoníaco puede **desorberse** mediante los procesos expuestos en el **capítulo 8**, pero entonces el amoníaco no se obtiene en forma pura, porque se mezcla con el vapor de agua y el aire. Por otra parte, aplicando calor, es posible evaporar parcialmente la solución y crear, de esta forma, una fase gaseosa que consta únicamente de agua y amoníaco. Y puesto que el gas es más rico en amoníaco que el líquido residual, se ha logrado cierto grado de separación. Mediante la **manipulación** adecuada de las fases, o mediante evaporaciones y condensaciones repetidas, es generalmente posible lograr una separación tan completa como se quiera y recobrar, en consecuencia, los dos componentes de la mezcla con la pureza deseada.

Son claras las ventajas de un método de **separación** como éste. En la **destilación**, la nueva fase difiere de la original por su contenido calorífico, pero el calor se incrementa o se elimina sin dificultad; por supuesto, debe considerarse inevitablemente el costo de aumentarlo o eliminarlo. Por otra parte, las operaciones de absorción o **desorción**, que dependen de introducir una sustancia **extraña**, proporcionan una nueva solución, que a su vez quizá tendría que separarse mediante alguno de los procesos difusivos, a menos que la nueva **solución** fuera útil directamente.

Al mismo tiempo, la destilación posee ciertas limitaciones como proceso de **separación**. En la **absorción** u operaciones similares, en donde se ha acordado introducir una sustancia **extraña** para obtener una nueva fase con fines de **distribución**, generalmente se escoge entre una gran variedad de disolventes con el fin de obtener la mayor separación posible. Por ejemplo, como el agua no sirve para absorber gases de hidrocarburos presentes en una mezcla gaseosa, se escoge, en lugar del agua, un aceite de hidrocarburo que proporcione una solubilidad elevada. Sin embargo, en la **destilación** no se tiene esta posibilidad de elección. El gas, que puede crearse a partir de un líquido mediante la aplicación de calor, consta, inevitablemente, sólo de los componentes que se encuentran en el líquido. Por lo tanto, ya que el gas es químicamente muy similar al líquido, el cambio de composición resultante por distribuir los componentes entre las dos fases generalmente no es muy grande. Es más, en algunos casos, el cambio de composición es tan pequeño que el proceso no es práctico; **más** aún, puede suceder que no haya ningún cambio en la composición.

No obstante, la separación directa que comúnmente es posible por destilación, en productos puros que no requieren procesamiento posterior, tal vez ha hecho de ésta la más importante de todas las operaciones de transferencia de masa.

EQUILIBRIO VAPOR-LÍQUIDO

Los métodos de destilación se aplicarán con éxito si se comprenden los equilibrios que existen entre la fase vapor y líquido de las mezclas encontradas. Por lo tanto, es esencial un breve análisis de dichos equilibrios. Aquí se **dará** especial **atención** a las mezclas binarias.

Diagrama de fases presión-temperatura-concentración

Inicialmente, se van a considerar las mezclas binarias, las cuales serán llamadas "ordinarias", para indicar (a) que los componentes líquidos se disuelven en cualquier proporción para formar soluciones homogéneas, las cuales no son necesariamente ideales, y (b) que no hay complicación alguna de puntos de ebullición máximos o mínimos. El componente A de la mezcla binaria A-B se considerará como el más volátil; esto significa que la presión de vapor de A puro a cualquier

temperatura es mayor que la presión de vapor B puro. Por supuesto, el equilibrio entre vapor-líquido para cada sustancia pura de la mezcla es su relación entre la presión de vapor y la temperatura, tal como se indican en la figura 7.1. Respecto de las mezclas binarias, se debe también considerar una variable adicional, la concentración. Las fracciones mol son las unidades mas convenientes de concentración que pueden utilizarse; durante todo este análisis x será la fracción mol de la sustancia más volátil, A en el líquido, y y^* la correspondiente fracción mol en el equilibrio de A en el vapor.

La representación gráfica completa del equilibrio requiere un diagrama tridimensional como el de la figura 9.1 [29, 47]. La curva señalada p_A es la curva de presión de vapor de A; cae completamente en el plano de composición mas cercano a $x = 1.0$. La curva se extiende desde su punto crítico C_A hasta su punto triple T_A , pero las complicaciones de la fase sólida que no intervienen en las operaciones de destilación no se van a considerar. De manera parecida, la curva p_B es la presión de vapor de B puro, en el plano mas lejano a $x = 0$. Las regiones del líquido y del vapor en las composiciones entre $x = 0$ y 1.0 están separadas por una superficie doble que se extiende desde p_A hasta p_B . La forma de esta superficie doble se estudia más fácilmente considerando secciones a presiones y temperaturas constantes, ejemplos de los cuales se muestran en la figura.

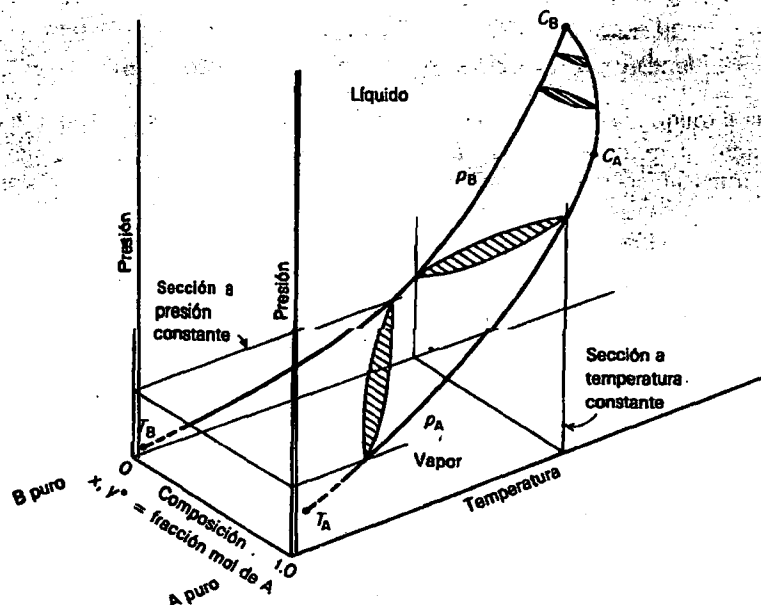


Figura 9.1 Equilibrios binarios vapor-líquido.

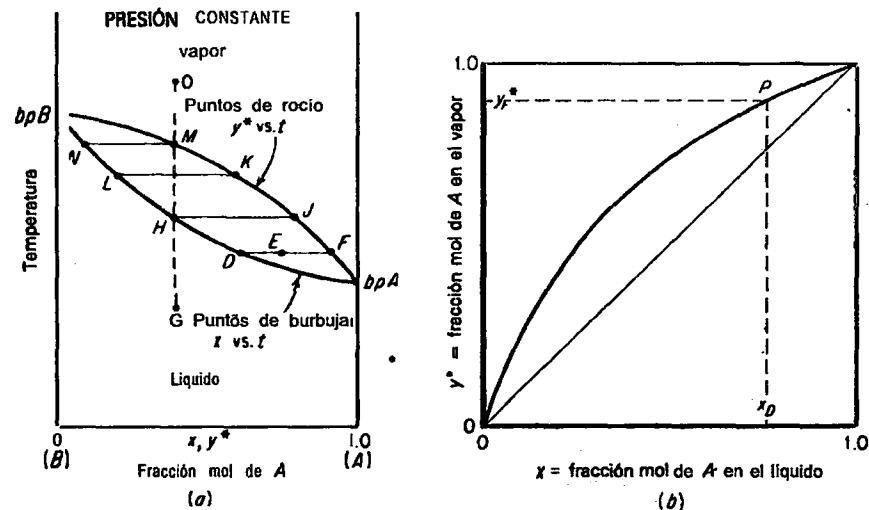


Figura 9.2 Equilibrios a presión constante vapor-líquido.

Equilibrios a presión constante

Considérese primero una sección típica a presión constante (figura 9.2a). La intersección de la superficie doble de la figura 9.1 con el plano de presión constante produce una curva sin máximos o mínimos que se extiende desde el punto de ebullición de B puro hasta el de A puro a la presión considerada. La curva superior proporciona la relación entre la temperatura y la composición del vapor (t - y^*); la curva inferior, la relación entre la temperatura y la composición del líquido (t - x). Las mezclas de líquido y vapor en el equilibrio están a la misma temperatura y presión, de forma que las líneas de unión, como la línea DF , unen las mezclas en el equilibrio en D y F . Hay un número infinito de dichas líneas de unión para este diagrama. Una mezcla en la curva inferior, como en el punto D , es un líquido saturado; una mezcla en la curva superior, como en F , es un vapor saturado. Una mezcla en E es una mezcla de dos fases, que consta de una fase líquida de composición en D y una fase vapor de composición en F , en proporción tal que la composición promedio de toda la mezcla se representa mediante E . Las cantidades relativas de las dos fases en el equilibrio están relacionadas con los segmentos de la línea de unión,

$$\frac{\text{Moles de } D}{\text{Moles de } F} = \frac{\text{línea } EF}{\text{línea } DE} \quad (9.1)$$

Considérese una solución en G , en un recipiente cerrado que puede mantenerse a presión constante moviendo un pistón. La solución está completamente líquida.

Si se calienta, la primera burbuja de vapor se forma en *H* y tiene la composición en *J*, más rica en la sustancia más volátil; por lo tanto, la curva inferior se llama la curva de temperatura del punto de burbuja. Al irse evaporando más mezcla, se forma más vapor a expensas del líquido; se origina entonces, por ejemplo, el líquido *L* y su vapor en el equilibrio *K*, aunque la composición de la masa total es aún la original como en *G*. La última gota del líquido se evapora en *M* y tiene la composición en *N*. El sobrecalentamiento de la mezcla sigue la trayectoria *MG*. La mezcla se ha evaporado en un rango de temperatura desde *H* hasta *M*, a diferencia de la temperatura única de evaporación de una sustancia pura. Entonces, el término **punto de ebullición** para una solución, generalmente no tiene significado puesto que la evaporación ocurre en un rango de temperatura, esto es, desde el punto de formación de la burbuja hasta el punto de formación de rocío. Si se enfría la mezcla en *O*, todos los fenómenos reaparecen en orden inverso. Por ejemplo, la condensación comienza en *M*, en donde la curva superior se conoce como la curva de punto de rocío y continúa hasta *H*.

Por otra parte, si una **solución** como la que se encuentra en *H*, se hierve en un recipiente abierto y sus vapores escapan hacia la atmósfera, el residuo líquido se volverá cada vez más pobre, puesto que el vapor es más rico en la sustancia más volátil. La temperatura y la **composición** del líquido saturado residual se mueven a lo largo de la curva inferior hacia *N*, al continuar la destilación.

Las composiciones vapor-líquido en el equilibrio pueden mostrarse también sobre un diagrama de composición (*x* vs. *y*^{*}), como en la figura 9.2*b*. Por ejemplo, el punto *P* sobre el diagrama representa la línea de unión *DF*. Dado que el vapor es más rico en la sustancia más volátil, la curva cae arriba de la diagonal 45° que se ha trazado como comparación.

Volatilidad relativa

Cuanto mayor es la distancia entre la curva en el equilibrio y la diagonal de la figura 9.2*b*, mayor es la diferencia en las composiciones del líquido y del vapor, y mayor es la facilidad para realizar la separación por **destilación**. Una medida numérica de lo anterior se conoce como el **factor de separación** o, particularmente en el caso de la destilación, la **volatilidad relativa** α . Esta es la relación entre la relación de concentraciones de A y B en una fase y en la otra, y es una medida de la posibilidad de **separación**.

$$\alpha = \frac{y^*/(1-y^*)}{x/(1-x)} = \frac{y^*(1-x)}{x(1-y^*)} \quad (9.2)$$

El valor de α generalmente cambiará al variar *x* de 0 a 0.1. si $y^* = x$ (excepto en $x = 0$ o 1), $\alpha = 1.0$ y la **separación** no es posible. Cuanto más arriba de la unidad esté α , mayor será el grado de separación.

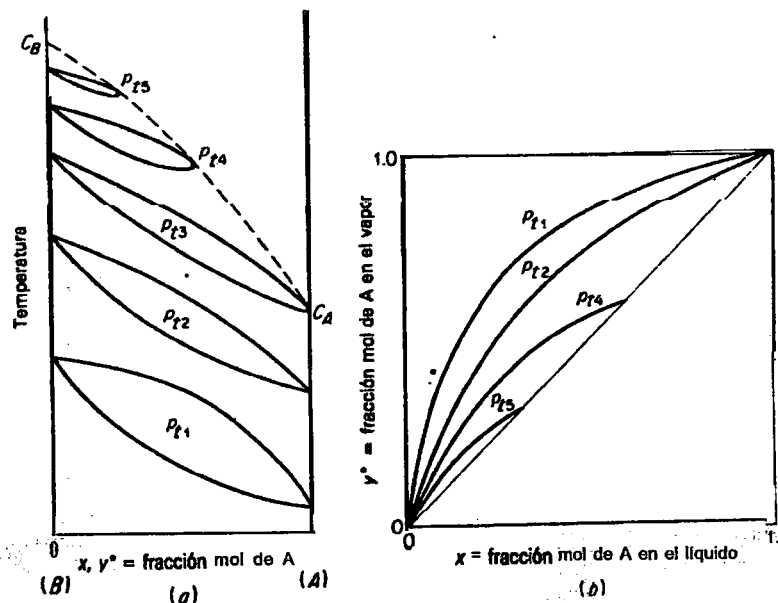


Figura 9.3 Equilibrios vapor-líquido a presiones aumentadas.

Presión aumentada

Por supuesto, a presiones mayores, las secciones a presión constante **intersecarán** la superficie doble de la figura 9.1 a temperaturas mayores. Las intersecciones se pueden proyectar en un plano sencillo, como en la figura 9.3*a*. Debe observarse

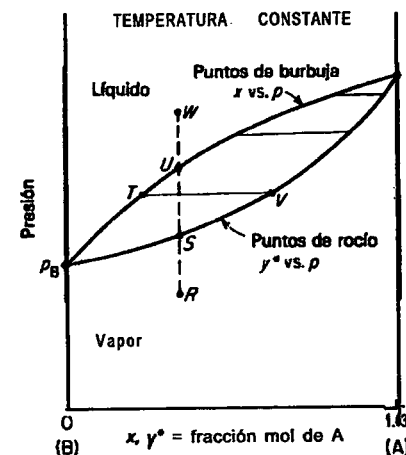


Figura 9.4 Equilibrios a temperatura constante vapor-líquido.

que las curvas anilladas no sólo se presentan a temperaturas altas, sino que generalmente también se vuelven más cerradas. Esto se ve claramente en las curvas de distribución correspondientes de la figura 9.3b. Por lo tanto, la volatilidad relativa y por ende la separabilidad, generalmente son menores a presiones elevadas. Cuando se supera la presión crítica de un componente, deja de existir la distinción entre vapor y líquido para ese componente y para mezclas, por lo tanto, las curvas anilladas se vuelven más cortas, como sucede a presiones mayores de p_c , que es la presión crítica para A en la figura. Las separaciones por destilación sólo pueden realizarse en la región en que exista una curva anillada.

En sistemas particulares, la presión crítica de la sustancia menos volátil puede alcanzarse antes que la presión crítica de la más volátil; también es posible que la superficie doble de la figura 9.1 se extienda, a composiciones intermedias, ligeramente más allá de las presiones críticas para cualquiera de las sustancias.

Equilibrios a temperatura constante

En la figura 9.4 se muestra una sección típica a temperatura constante del diagrama de fases tridimensional. La intersección del plano a temperatura constante con la superficie doble de la figura 9.1 proporciona las dos curvas que se extienden sin máximos ni mínimos desde la presión de vapor de B puro hasta la A. Al igual que antes, hay un número infinito de líneas de unión horizontales, como TV, que unen un vapor en el equilibrio, como en V, con su líquido correspondiente, como en T. Una solución en W, en un recipiente cerrado, es completamente un líquido; si la presión se reduce a temperatura constante, la primera burbuja de vapor se forma en U, la evaporación completa sucede en S; una reducción mayor de la presión da un vapor sobrecalentado como en R.

Los datos de equilibrio vapor-líquido, excepto en el caso de las situaciones especiales de las soluciones ideales y regulares, se deben determinar experimentalmente. Existen descripciones de métodos experimentales [18], extensas bibliografías [67] y listas de datos [7, 22].

Soluciones ideales. La Ley de Raoult

Antes de estudiar las características de las mezclas que se desvían marcadamente de las características que se acaban de describir, se van a considerar los equilibrios para el caso límite de las mezclas cuyos vapores y líquidos son ideales. La naturaleza de las soluciones ideales y los tipos de mezclas que se aproximan al ideal se analizaron en el capítulo 8.

Para una solución ideal, la presión parcial en el equilibrio $\bar{p}^*$ de un componente a una temperatura fija es igual al producto de su fracción mol en el líquido por su presión de vapor p cuando está puro a esta temperatura. Esta es la Ley de Raoult.

$$\bar{p}_A^* = p_A x \quad \bar{p}_B^* = p_B(1 - x) \quad (9.3)$$

Si la fase vapor también es ideal,

$$p_t = \bar{p}_A^* + \bar{p}_B^* = p_A x + p_B(1 - x) \quad (9.4)$$

y las presiones totales, al igual que las parciales, son lineales en x a una temperatura dada. Estas relaciones se muestran de modo gráfico en la figura 9.5. Entonces puede calcularse la composición del vapor en el equilibrio a esta temperatura. Por ejemplo, el valor de y^* en el punto D sobre la figura es igual a la relación entre las distancias FG y EG,

$$y^* = \frac{\bar{p}_A^* x}{p_t} \quad (9.5)$$

$$1 - y^* = \frac{\bar{p}_B^*}{p_t} = \frac{p_B(1 - x)}{p_t} \quad (9.6)$$

Sustituyendo en la ecuación (9.2), la volatilidad relativa α es

$$\alpha = \frac{p_A}{p_B} \quad (9.7)$$

Por tanto, para soluciones ideales es posible calcular los equilibrios totales vapor-líquido a partir de las presiones de vapor de las sustancias puras. Con presiones demasiado elevadas como para aplicar la ley de los gases ideales, se utilizan fugacidades en lugar de presiones [29, 42]. También es posible calcular los equilibrios para la clase especial de soluciones conocidas como "regulares" [21]. Sin embargo, en todas las demás mezclas es necesario obtener los datos experimentalmente.

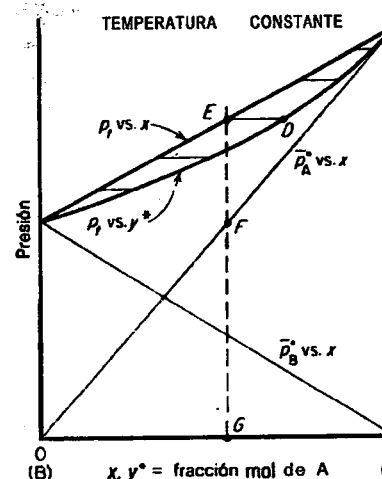


Figura 9.5 Soluciones ideales.

OPERACIÓN DE UNA SOLA ETAPA-EVAPORACIÓN INSTANTÁNEA

La evaporación instantánea o destilación en el equilibrio —como algunas veces se llama—, es una operación de una sola etapa en donde se evapora parcialmente una mezcla líquida, se permite que el vapor alcance el equilibrio con el líquido residual y se separan y eliminan del aparato las fases vapor y líquido resultante. Puede llevarse a cabo por lotes o en forma continua.

El producto, D moles/tiempo, más rico en la sustancia más volátil, es en este caso totalmente un vapor. El balance de materia y el de entalpía son:

$$F = D + W \quad (9.1)$$

$$Fz_F = Dy_D + Wx_W \quad (9.2)$$

$$FH_F + Q = DH_D + WH_W \quad (9.3)$$

Resolviendo estas ecuaciones simultáneamente, se tiene

$$-\frac{W}{D} = \frac{y_D - z_F}{x_W - z_F} = \frac{H_D - (H_F + Q/F)}{H_W - (H_F + Q/F)} \quad (9.4)$$

Sobre el diagrama Hxy esto representa una línea recta a través de los puntos de coordenadas (H_D, y_D) que representan a D , (H_W, x_W) que representan a W y $(H_F + Q/F, z_F)$ que representa la mezcla de alimentación después que abandona el intercambiador de calor de la figura 9.13. En la parte superior de la figura 9.14

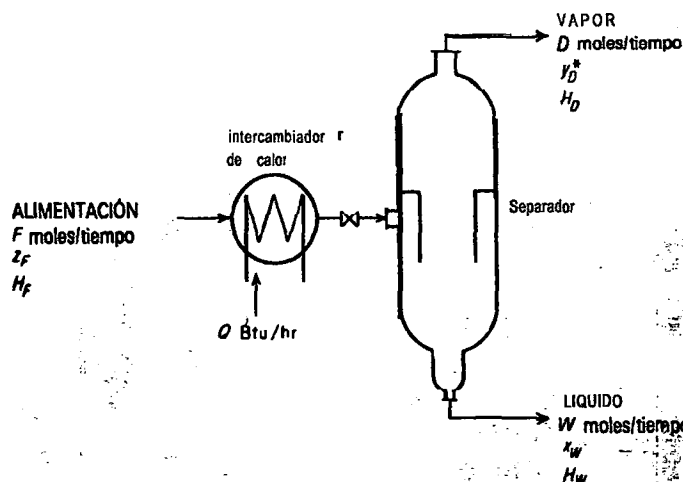


Figura 9.13 Evaporación instantánea continua.

En la figura 9.13 se muestra de modo esquemático un diagrama típico de flujo para la operación continua. Aquí, el líquido alimentado se calienta en un intercambiador de calor tubular tradicional o pasándolo a través de los tubos calientes de un horno de combustible. Entonces, se reduce la presión, el vapor se forma adiabáticamente a expensas del líquido y la mezcla se introduce en un tanque de separación vapor-líquido. El separador que se muestra es del tipo ciclón, en donde la alimentación se introduce tangencialmente en un espacio anular cubierto. La parte líquida de la mezcla se arroja mediante fuerza centrífuga hacia la pared externa y sale por el fondo, mientras que el vapor sube a través de la chimenea central y sale por la parte superior. Entonces, el vapor puede pasar a un condensador, el cual no se muestra en la figura. En particular para la evaporación instantánea de una sustancia volátil a partir de una sustancia relativamente no volátil, la operación en el separador puede llevarse a cabo a presión reducida, pero no tan baja que el agua ordinaria de enfriamiento no condense el producto evaporado.

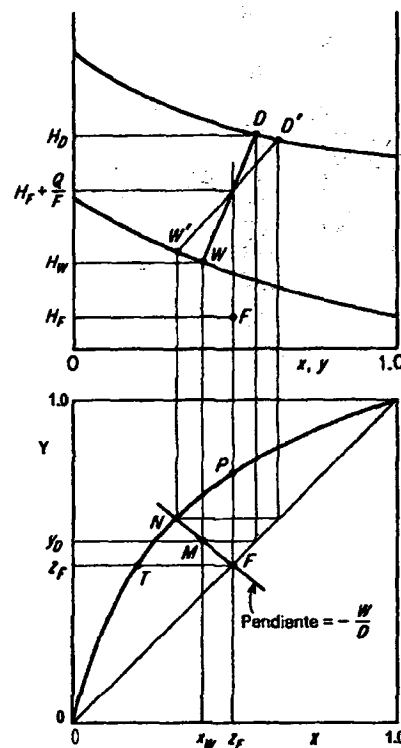


Figura 9.14 Evaporación instantánea.

esto se muestra como la línea DW . Los dos miembros del lado izquierdo de la ecuación (9.34) representan la línea usual de **operación** en una sola etapa sobre las coordenadas de distribución, con pendiente negativa como para todas las operaciones de una sola etapa (a corriente paralela) (véase el capítulo 5), pasando a través de las composiciones que representan a las corrientes entrante y saliente, puntos F y M sobre la figura inferior. Si las corrientes efluentes estuviesen en equilibrio, el dispositivo sería una etapa ideal y los productos D' y W' estarían sobre una línea de unión en la figura superior y sobre la curva en el equilibrio en N en la figura inferior. El vapor más rico, pero en cantidad infinitesimal, es el correspondiente a P en el punto de burbuja de la mezcla alimentada; y el líquido más pobre, también en cantidad infinitesimal, es el correspondiente a T en el punto de rocío de la mezcla alimentada. Las composiciones de los productos reales estarán entre estos límites, según el grado de **evaporación** de la mezcla alimentada y la eficiencia de la etapa.

Condensación parcial

Todas las ecuaciones se aplican igualmente bien para el caso en que la mezcla alimentada sea un vapor y en que se tome como negativo Q , el calor eliminado en el **intercambiador** de calor para producir la condensación incompleta. En la parte superior de la figura 9.14, el punto F es entonces o bien un vapor saturado, o bien un vapor sobrecalentado.

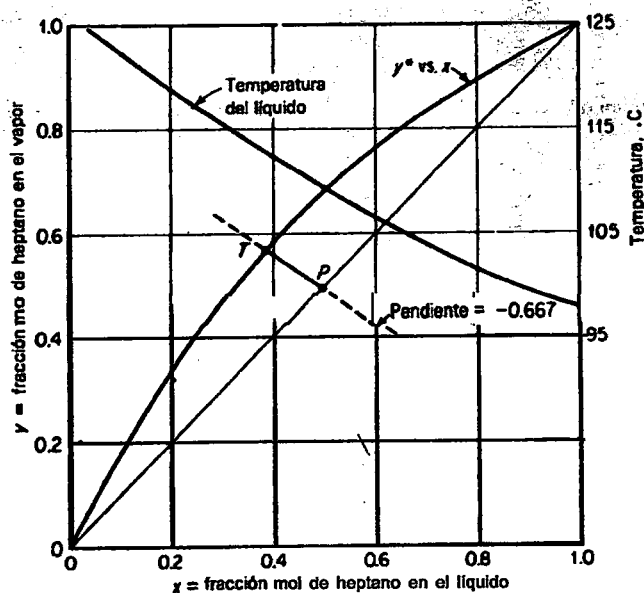


Figura 9.15 Solución al ejemplo 9.4.



United States Patent [19]
Chao

[11] Patent Number: **5,145,658**
[45] Date of Patent: **Sep. 8, 1992**

[54] **RECLAIMING OF HEAT OF REACTION ENERGY FROM AN ALKALINE SCRUBBING SOLUTION USED IN ACID GAS REMOVAL PROCESSES AND APPARATUS THEREFOR**
[75] Inventor: **I-Meen Chao, Overland Park, Kans.**
[73] Assignee: **Eickmeyer & Associates, Inc., Overland Park, Kans.**
[21] Appl. No.: **755,689**
[22] Filed: **Sep. 6, 1991**

4,409,191 10/1983 Osman 423/228

OTHER PUBLICATIONS

Olsen, John C. Unit Processes & Principles of Chemical Engineering, D. Van Nostrand Company 1932 pp. 1-3.

Primary Examiner—Gary P. Straub
Attorney, Agent, or Firm—Hovey, Williams, Timmons & Collins

ABSTRACT

A process and apparatus is disclosed for reclaiming of heat of reaction energy from an alkaline scrubbing solution used in acid gas removal processes and apparatus therefor. The heat recovered is used to produce steam which may then be employed to assist in steam stripping the rich scrubbing solution to effect regeneration thereof. The rich scrubbing solution containing heat of reaction thermal energy is passed through a rich-reflux reboiler to recover a part of the energy to produce at least a part of the stripping steam, and then through a rich-lean reboiler under a reduced pressure to produce additional quantities of stripping steam. A reduction in steam requirements for regeneration of the rich alkaline scrubbing agent of at least 10% is thereby realized.

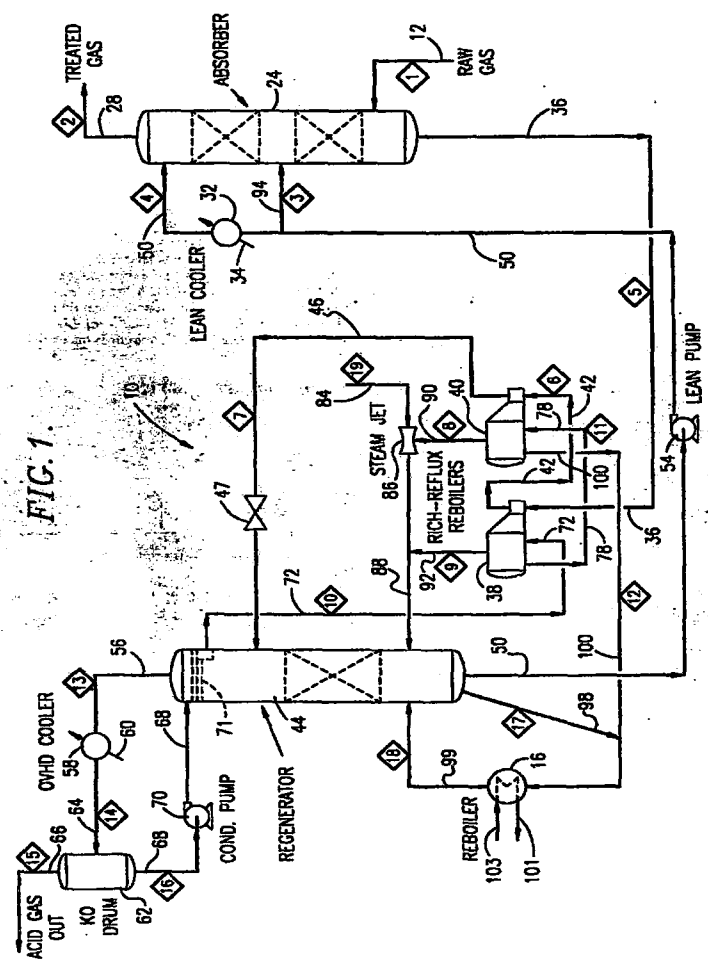
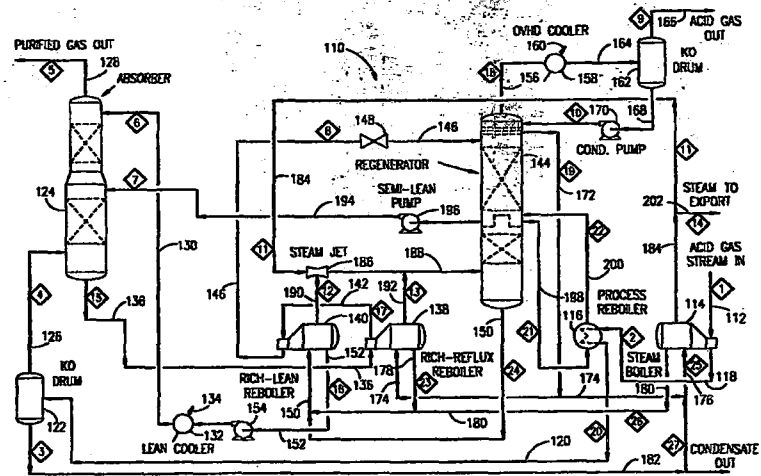
Related U.S. Application Data
[63] Continuation-in-part of Ser. No. 619,246, Nov. 28, 1990, abandoned.
[51] Int. Cl.⁵ **C01B 17/16; C01B 31/20; B01D 50/00**
[52] U.S. Cl. **423/232; 423/228; 423/DIG. 6; 422/168; 422/173**
[58] Field of Search **423/DIG. 6, 223, 228, 423/229, 232, 242, 243; 422/168, 173**

References Cited

U.S. PATENT DOCUMENTS

3,851,041 11/1974 Eickmeyer 423/223
4,160,810 7/1979 Benson et al. 423/223

21 Claims, 2 Drawing Sheets



RECLAIMING OF HEAT OF REACTION ENERGY FROM AN ALCALINE SCRUBBING SOLUTION USED IN ACID GAS REMOVAL PROCESSES AND APPARATUS THEREFOR

This is a continuation-in-part application of an application filed Nov. 28, 1990 as Ser. No. 07/619,246 abandoned.

BACKGROUND OF THE INVENTION

1. Field of the Invention
This invention relates generally to processes and equipment for removal of acid gases, such as CO₂ and H₂S, from gas streams. In particular, the invention relates to an improved method and apparatus for reclaiming heat from the rich alkaline scrubbing solution which has been used to absorb the acid gases contained in the gaseous mixture.

2. Overview
Absorption of an acid gas by an alkaline scrubbing agent causes the rich scrubbing solution temperature to increase by virtue of the heat of reaction between the acid gas and the alkaline agent. However, absorption of the acid gas by the scrubbing solution lowers its boiling point. As a consequence, when the rich scrubbing solution is introduced into the regenerator where it is subjected to steam stripping, a significant amount of water and acid gas in the rich scrubbing solution flashes and goes overhead from the lower boiling point scrubbing solution. Flash of water vapor and acid gas from the rich solution results in significant loss of energy from the rich scrubbing solution that would otherwise be available to produce steam for steam stripping makeup, or for export.

The present process therefore, provides an improved method and apparatus for recovering heat of reaction energy from the rich scrubbing solution in a manner which precludes significant loss of energy from the alkaline scrubbing agent as a result of water vapor and acid gas flash from the rich scrubbing solution when it is introduced into the regenerator.

3. Description of the Prior Art
Processes and equipment are well known for removing CO₂ and/or H₂S from gas streams which contain such acid gases. There are various liquid, solid and chemical sources of gas mixtures that contain acid gases. Sour natural gas is one source. The gas mixture resulting from enhanced oil recovery processes which utilize CO₂ also includes a quantity of acid gases. In addition, the low temperature shift effluent from a steam reforming reaction associated with an ammonia plant, contains substantial quantities of carbon dioxide and/or hydrogen sulfide. The process off gas in this instance has the processing equipment at a relatively high temperature and pressure, and usually contains significant amounts of steam as well. Many partial oxidation reactions also produce a gaseous effluent containing acid gases.

The acid gases are removed from the gas stream by absorption of the CO₂ and/or H₂S in a hot aqueous alkaline scrubbing medium such as potassium carbonate, which is then regenerated by steam stripping. After passage of the gaseous mixture through the scrubber containing an alkaline scrubbing agent, the purified gas goes overhead while the rich scrubbing solution underflow is returned to a regenerator for steam stripping thereof.

The process of removing CO₂ and/or H₂S from gas streams containing these acid gases can be made more efficient if thermal energy is recovered from the absorption medium in order that the reclaimed heat can be used to produce steam for use in regeneration of the hot alkaline scrubbing agent. Reduction of the regeneration heat requirements has been a much sought after goal. Production of significant quantities of steam over and above that required for steam stripping of the rich scrubbing solution to provide export steam represents a further advantageous result.

Elckmeyer in U.S. Pat. Nos. 3,932,582, 3,851,041 and 4,271,132 issued in 1976, 1974 and 1981 respectively taught that process waste heat contained in the raw gas stream may be recovered by condensing most of the steam before the gas stream is introduced into an absorber containing an alkaline absorption agent. Elckmeyer, however, did not suggest recovery of heat from the rich scrubbing solution leaving the absorber.

U.S. Pat. Nos. 3,823,222 to Benson, and No. 4,160,810, issued to Benson and McCray also teach that steam may be recovered from the hot process gas prior to passage of such gas through an alkaline absorption scrubber for use in stripping the rich scrubbing solution leaving the absorber. In these patents, the hot rich scrubbing solution is sent directly from the absorber to the regenerator with no suggestion being made that waste heat can efficiently be removed from that solution.

Osman in U.S. Pat. No. 4,009,191 teaches a cyclic process for the removal of acid gases from a feed gas stream comprising a hot, alkaline scrubbing solution by means of an aqueous recycled between an absorber in which acid gases are absorbed by scrubbing solution and a regenerator wherein acid gases are desorbed by steam stripping. Stripping steam is at least partially derived from the hot, steam-containing gas mixture. Condensation and separation of the steam content of the hot process gas is carried out before the gas mixture enters the absorber. However, the Osman process does not teach or suggest reclaiming of heat from the rich scrubbing solution that is derived from the heat of reaction of the acid gas with the scrubbing agent and makes no mention of using such steam as a part of the steam makeup for stripping of the rich scrubbing solution introduced into the regenerator.

SUMMARY OF THE INVENTION

The efficiency of an alkaline agent acid gas removal process is enhanced in accordance with this invention by recovery of a substantial part of the heat of reaction energy contained in the rich scrubbing solution before delivery of the rich solution to the regenerator. The recovered energy may be in the form of steam which is used to supplement the steam requirements of the rich alkaline agent regenerator, or as steam that may be exported to another use in the process facility or sold to third parties.

The exothermic reaction of the acid gas with the alkaline scrubbing agent causes the temperature of the scrubbing solution to increase. In most instances, the temperature of the rich scrubbing solution is raised to a level of at least about 180° F. Reclaiming of the acid gas with the alkaline scrubbing agent only adds to the heat content of the alkaline scrubbing solution, but there is also a concomitant lowering of the boiling point of the scrubbing agent, depending upon the degree of

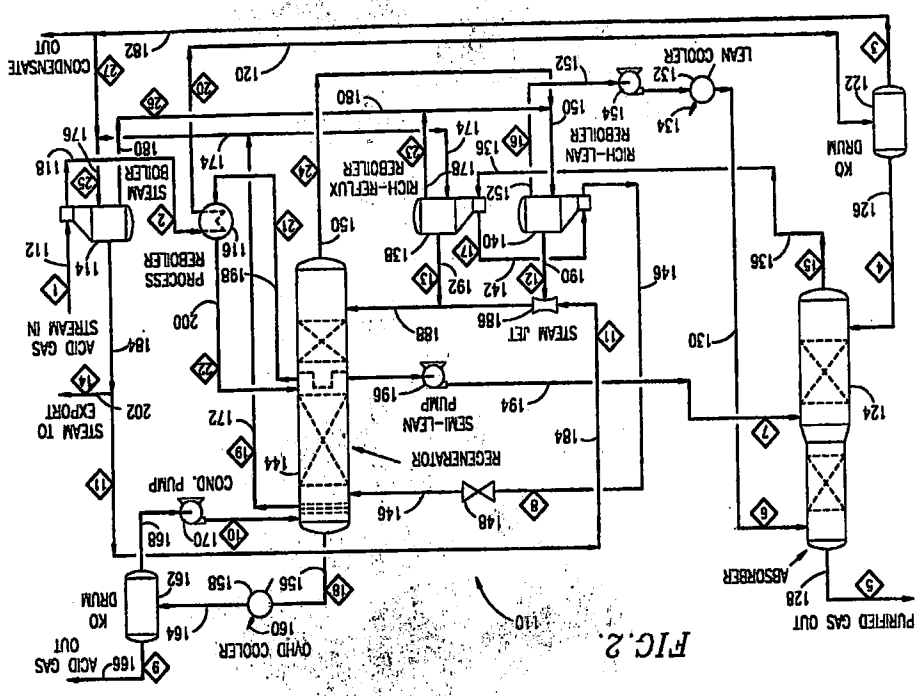


FIG. 2

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OPERATION

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For a better understanding of the operation of apparatus 10, the box score of Example 1 hereunder sets forth a representative material balance for a typical process which may be advantageously carried out in accordance with the present invention to purify a gas stream containing an acid gas such as CO₂. It is to be understood in this respect that the specific process only set out in the box score are for exemplary purposes only to illustrate the degree of heat recovery obtainable by scrubbing solution that may be obtained through the process. The exothermic reaction between the acid gas and the alkaline scrubbing agent produces significant amounts of thermal energy in the rich scrubbing solution compared with the lean scrubbing solution. In prior processes, this heat has been lost and has not been available for use in heating the scrubbing solution, or to provide additional export steam. Incorporation of rich-reflux boilers 38 and 40 and rich in the present process permits advantageous recovery of a substantial part of the heat of reaction thermal energy contained in the rich scrubbing solution exiting from absorber 24. An especially important feature of the process is the use of steam jet 86 which has an input port connected to rich-reflux boiler 40 to thereby lower the pressure in the reboiler and permit recovery of steam in a more efficient manner by decreasing the temperature approach required between the liquid inputs into reboilers 38 and 40 in order to obtain efficient heat transfer.

For convenience, the streams of the illustrative process as set out in the schematic representation of FIG. 4 are keyed to the box score of Example 1 by reference within a diamond in the description hereof, the stream coded by a diamond in the drawing are identified as "S-a" wherein "S" represents "stream" and "a" is the number assigned to that stream in the box score.

EXAMPLE 1														
Stream #	S-1	S-2	S-3	S-4	S-5	S-6	S-7	S-8	S-9	S-10	S-11	S-12	S-13	S-14
Press. P.s.i.	515.0	510.0	320.0	320.0	310.0	310.0	220.0	219.4	213.3	210.0	200.0	200.0	200.0	200.0
Temp. °F.	240.0	240.0	240.0	240.0	211.0	241.0	0	0	169.7	169.7	0	0	0	0
Comp. Btu/lb.	162796	113131	0	0	0	0	0	0	0	0	0	0	0	0
N ₂	172.26	172.26	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
O ₂	2173.16	2173.16	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
CO ₂	785.82	785.82	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
H ₂ O	387.58	387.58	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
CO ₂	1200.00	12.08	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
H ₂ O	77.34	71.71	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Steam	5483.00	4698.40	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Sp. Gr. @ 70° F.	—	—	1.181	1.204	1.176	1.176	1.180	1.189	—	—	—	—	—	—
Comp. Btu/lb.	—	—	1285787	175744	1516012	1516012	1516012	1516012	—	—	—	—	—	—
K ₂ CO ₃	0.00	0.00	1512.73	206.28	531.09	531.09	531.09	531.09	0.00	0.00	0.00	0.00	0.00	0.00
KHCO ₃	0.00	0.00	1635.29	224.17	567.17	567.17	567.17	567.17	0.00	0.00	0.00	0.00	0.00	0.00
H ₂ O	0.00	0.00	3200.00	6941.97	56617.35	56617.35	56617.35	56617.35	0.00	0.00	0.00	0.00	0.00	0.00
TOTAL	0.00	0.00	54069.48	7705.40	61375.51	61375.51	61375.51	61375.51	0.00	0.00	0.00	0.00	0.00	0.00

EXAMPLE 1

EXAMPLE 1										
Stream #	S-10	S-11	S-12	S-13	S-14	S-15	S-16	S-17	S-18	S-19
Press. P.s.i.	213.3	213.3	179.0	210.0	210.0	210.0	200.0	200.0	213.3	200.0
Temp. °F.	210.0	206.0	210.0	211.0	211.0	184.0	184.0	184.0	213.3	200.0
Comp. Btu/lb.	0	0	0	0	94452	69412	69412	0	31887	17024
N ₂	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
O ₂	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
CO ₂	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
H ₂ O	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
CO ₂	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Steam	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Sp. Gr. @ 70° F.	—	—	—	—	—	—	—	—	—	—
Comp. Btu/lb.	—	—	—	—	—	—	—	—	—	—

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ing solution in the rich-reflux reboiler and the rich-lean end, steam is introduced into the lower part of regenerator tower 44 through line 88 that is connected to a source line 84. It can be seen from FIG. 1 that it is preferred that line 84 be connected to an inlet of a steam jet 86. The other inlet of jet 86 is connected to the shell side of reboiler 40 by a line 90. Passage of steam through jet 86 from line 84 to line 90 causes reduced pressure to exist at the inlet of the jet having line 90 connecting thereto, thus lowering the pressure inside of the shell side of reboiler 40. A line 92 serves to connect the shell side of reboiler 38 directly with line 88.

Reclaimed acid gas which includes a quantity of water vapor exits from regenerator tower 44 through line 56 which leads to overhead cooler 38. The outlet of cooler 38 is joined to knock out drum 62 by a line 64. Cooling water is delivered to cooler 38 via line 60. After removal of substantial water from the acid gas stream in knock out drum 62 the dehumidified acid gas is directed to storage or use through discharge line 64. Water removed from the acid gas in knock out drum 62 exits from the knock out drum through line 68 having a condensate pump 70 interposed therein. Line 68 is joined to the upper end of regenerator tower 44 above the demister which collects in the upper end of absorber 24. A part of the lean scrubbing solution which leaves reboiler 44 exits therefrom through line 72. Line 78 connects the lower end of reboiler 38 through line 74. Line 78 connects the shell side of reboiler 38 with the shell side of reboiler 40. A part of the lean scrubbing solution which leaves reboiler tower 44 exits therefrom via line 98 which joins with line 100 extending from the shell side of reboiler 40 to the inlet of reboiler 16. The outlet of reboiler 16 is connected to the lower end of regenerator tower 44 by a line 99. Steam or a hot liquid available from other parts of a process facility is introduced into reboiler 16 through supply and return lines 101 and 103.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENT

Preferred apparatus for reclaiming heat from a rich alkaline scrubbing solution which has been used to absorb acid gases from a gaseous mixture employing the improved method of this invention is schematically illustrated in FIG. 1. The gaseous mixture is of the type wherein there is a need to remove acid gases contained therein such as CO₂ and/or H₂S. An exemplary gaseous mixture in this respect is one that results from the use of CO₂ containing gas streams present as a in enhanced oil recovery processes. Sour natural gas is another typical gas mixture wherein there is often a need to remove CO₂ and/or H₂S contained in the gaseous product. Natural gas from a well head can contain carbon dioxide in amounts as high as 50% or somewhat greater. Other sour gas streams may have levels of carbon dioxide of at least about 90%. These sour gas streams may also often contain hydrogen sulfide in conjunction with or instead of carbon dioxide.

In FIG. 1, the raw gas containing CO₂ and/or H₂S is directed to apparatus 10 via line 12 that is connected to the inlet at the lower part of an absorber 24 which receives a hot alkaline scrubbing agent such as potassium carbonate. Rich scrubbing solution leaves absorber tower 24 through line 36 connected to rich-reflux reboiler 38 and leading to the tube side of rich-reflux boiler 38. The rich solution leaves reboiler 38 via line 42 in turn connected to the tube side of rich-reflux reboiler 40. The outlet of the tube side of reboiler 40 is connected to the upper section of alkaline scrubbing solution regenerator 44 through line 46. The medium of a line 46, valve 47 interposed in line 46 permits selective control of the flow therethrough.

Regenerator tower 44 has an outlet line 50 connected to the bottom of absorber 24 which leads to the upper end of absorber 24. A pump 54 is provided in line 50 for directing the lean alkaline scrubbing solution into the absorber 24 under a suitable pressure. A cooler 32 which receives cooling water via line 24 serves to lower the temperature of the lean scrubbing solution to a predetermined value before delivery of the lean solution into the top of absorber tower 24. Bypass line 94 permits a certain proportion of the lean solution to be directed into the central part of absorber tower 24 between the packing sections therein in bypassing relationship through cooler 32. Purified gas exits from absorber 24 through line 28.

conversion of the alkaline agent. For example, if the scrubbing agent is potassium carbonate, reaction of an acid gas with the potassium carbonate converts the latter to potassium bicarbonate, a typical absorption system, the lean absorbent and acid gas may contain, for example, about 70% K₂CO₃ and about 30% KHCO₃. When a gas stream containing an acid gas is passed through an alkaline scrubber, reaction of the acid gas with the carbonate solution results in conversion of up to about 90% of the carbonate, thus leaving about 10% K₂CO₃.

The steam and acid gas(es) leaving the top of the regenerator pass through a cooler which produces a condensate. This condensate is directed to one side of a rich-reflux reboiler for indirect heat exchange with the rich scrubbing solution leaving the absorber at a temperature above about 180° F. Secondary steam produced in the rich-reflux reboiler is mixed with steam introduced into the regenerator for stripping of the rich scrubbing solution delivered to the regenerator. After leaving the rich-reflux reboiler and before introduction into the regenerator, the rich scrubbing solution is directed through one side of a rich-lean reboiler which also receives on the other side thereof, the condensate leaving the rich-reflux reboiler.

In those instances where the gas mixture undergoing treatment for removal of acid gas(es) therefrom also includes steam, recovery of steam through provision of the rich-lean reboiler apparatus for recovering heat from the rich scrubbing solution may be enhanced by reclaiming of steam from the raw process gas. Steam produced as a result of heat and/or acid recovery from the process gas stream may be delivered to the shell side of the rich-lean reboiler. In this manner, the primary steam may be produced which is added to the primary steam and secondary steam stripping of the regenerator. In accordance with the present embodiment of the invention, the rich scrubbing solution at a temperature above and at least 240° F. is brought into heat exchange relationship with condensate at a temperature no greater than 230° F.

Recovery of the heat of reaction energy from the rich scrubbing solution reduces, if not totally eliminates, the need for import steam requirements, or burning of fuel to produce the steam required for regeneration of the scrubbing agent. The process described in so efficient that when a significant amount of waste heat in the form of steam is also recovered from the raw process gas, as well as the heat of reaction energy produced in the absorber, the steam available is so abundant that in many instances, steam is actually available for export to other parts of the process.

Removal of heat from the rich scrubbing solution before regeneration thereof also has the related advantage of lowering the temperature of the scrubbing solution before introduction of the scrubbing medium into the regenerator which limits the amount of water vapor and acid gas which flashes in the regenerator. A substantial amount of heat is therefore recovered from the rich scrubbing solution that would otherwise be lost by flash of water vapor and/or acid gases from the solution by virtue of its lowered boiling point.

In order to assure adequate efficiency of recovery of waste heat to produce steam for further use thereof, either in regeneration of the alkaline scrubbing agent, or for export, it is necessary that the temperature approach difference between the condensate and the rich scrub-

-continued-

EXAMPLE 2														
Stream #	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
TOTAL	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Stream #	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Press, psi	22.0	22.0	22.0	22.0	22.0	22.0	22.0	22.0	22.0	22.0	22.0	22.0	22.0	22.0
Temp, °F	22.0	22.0	22.0	22.0	22.0	22.0	22.0	22.0	22.0	22.0	22.0	22.0	22.0	22.0
Comp. lb/mph	0	0	0	0	0	0	0	0	0	0	0	0	0	0
H ₂	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
N ₂	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Ar	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
CO ₂	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
CO	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
CH ₄	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Water	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
TOTAL	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
By Gr. @ PT	27000	27000	27000	27000	27000	27000	27000	27000	27000	27000	27000	27000	27000	27000
Comp. lb/mph	1.184	1.184	1.184	1.184	1.184	1.184	1.184	1.184	1.184	1.184	1.184	1.184	1.184	1.184
K ₂ CO ₃	292.16	292.16	292.16	292.16	292.16	292.16	292.16	292.16	292.16	292.16	292.16	292.16	292.16	292.16
H ₂ O	10882.88	10882.88	10882.88	10882.88	10882.88	10882.88	10882.88	10882.88	10882.88	10882.88	10882.88	10882.88	10882.88	10882.88
TOTAL	11270.39	11270.39	11270.39	11270.39	11270.39	11270.39	11270.39	11270.39	11270.39	11270.39	11270.39	11270.39	11270.39	11270.39

From the above example, it can be seen that in the illustrative instance where raw gas stream S-1 is brought into system 110 via line 112 at a temperature of about 450° F. and at 419 psia, the stream S-2 leaving such reboiler may for example be lowered to a temperature of 313° F. at a pressure of 414 psia. Indirect heat exchange of the raw gas against water condensate introduced via stream S-25 at 200° F. and made up of water 30 condensate stream S-27 from drum 122 applied via line 182, and water condensate stream S-19 from the top of reboiler column 44 furnished via line 172, produces steam at 298° F. and 65 psia identified as stream S-11 which is directed to steam jet 186 via line 184, and 35 through line 188.

The overhead gas at an exemplary temperature of 238.6° F. and under a pressure of 409 psia leaves knock-out drum 122 in the form of stream S-4 which is conveyed via line 126 to the lower part of reboiler column 124. The raw gas containing CO₂ and/or H₂S brought into contact with a hot aqueous alkaline scrubbing solution such as potassium carbonate in the form of stream S-6 introduced via line 128, the scrubbing agent in the example given is at a temperature of 180° F. and a pressure of 420 psia.

In the illustrative example, the rich scrubbing solution leaving absorber 124 as stream S-15 is at a temperature of 245° F. and under a pressure of 409 psia. That stream is directed into the tube side of rich-reflux boiler 138 for heat exchange with condensate from stream S-19 supplied to the shell side of the reboiler 138. The condensate, at a temperature of 200° F. and under a pressure of 20.5 psia, enters the shell side of reboiler 138 by gravitational flow. Indirect heat exchange between the condensate and the rich scrubbing solution in reboiler 138 produces a quantity of steam which is directed to line 188 in the form of stream S-13 which can be seen from the exemplary table above is at 234.3° F. and under a pressure of 22.5 psia. It is evident from the box score that the temperature approach between the rich scrubbing solution and the condensate supplied to rich-reflux reboiler is in the order of +25° F. This results in significant steam being produced in the reboiler for use as alkaline agent regenerating steam. For example, in the table, the steam produced in reboiler 138

EXAMPLE 2

Stream #	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9	1.0
Press, psi	480.0	480.0	480.0	480.0	480.0	480.0	480.0	480.0	480.0	480.0
Temp, °F	480.0	480.0	480.0	480.0	480.0	480.0	480.0	480.0	480.0	480.0
Comp. lb/mph	794.972	348.079	0	2158.83	84.831	0	0	0	131.502	0
H ₂	730.67	730.67	0.00	730.67	730.67	0.00	0.00	0.00	0.00	0.00
N ₂	2292.99	2292.99	0.00	2292.99	2292.99	0.00	0.00	0.00	0.00	0.00
Ar	29.40	29.40	0.00	29.40	29.40	0.00	0.00	0.00	0.00	0.00
CO ₂	37.86	37.86	0.00	37.86	37.86	0.00	0.00	0.00	0.00	0.00
CO	287.44	287.44	0.00	287.44	287.44	0.00	0.00	0.00	0.00	0.00
H ₂ O	5472.75	5472.75	0.00	5472.75	5472.75	0.00	0.00	0.00	0.00	0.00
TOTAL	17314.55	17314.55	0.00	17314.55	17314.55	0.00	0.00	0.00	0.00	0.00
Liquid, lb/h	0	0	0	0	0	0	0	0	0	0
Comp. lb/mph	0	0	0	0	0	0	0	0	0	0
K ₂ CO ₃	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
H ₂ O	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
TOTAL	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
By Gr. @ PT	2538.79	2538.79	0.00	2538.79	2538.79	0.00	0.00	0.00	0.00	0.00
Comp. lb/mph	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
K ₂ CO ₃	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
H ₂ O	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
TOTAL	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Stream #	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9	1.0
Press, psi	284.0	284.0	284.0	284.0	284.0	284.0	284.0	284.0	284.0	284.0
Temp, °F	473.8	473.8	473.8	473.8	473.8	473.8	473.8	473.8	473.8	473.8
Comp. lb/mph	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
H ₂	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
N ₂	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Ar	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
CO ₂	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
CO	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
CH ₄	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Water	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
TOTAL	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
By Gr. @ PT	2628.25	2628.25	0.00	2628.25	2628.25	0.00	0.00	0.00	0.00	0.00
Comp. lb/mph	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
K ₂ CO ₃	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
H ₂ O	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
TOTAL	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00

turned to line 174 via line 182. The remaining condensate is sent to the steam generation system, or other use, of such condensate.

Steam recovered from the raw process gas in the shell side of steam boiler 114 is directed from an outlet thereof via line 184 to the inlet side of a multi-orifice steam jet 186. The outlet side of the steam jet 186 is connected directly to the lower part of reboiler column 144 by a line 188. A line 190 communicates the vacuum port side of steam jet 186 with an outlet of the shell side of rich-reflux reboiler with line 188.

A semi-lean scrubbing solution line 194 interconnects an intermediate outlet of reboiler column 144 with an intermediate inlet of absorber column 124. Semi-lean pump 196 is interposed in line 194 between reboiler 144 and absorber 124 for returning semi-lean scrubbing solution to the central part of the absorber 124 from an intermediate zone of reboiler column 144.

Semi-lean scrubbing solution is also removed from the central part of reboiler column 144 via an outlet connected to line 198 which leads to an inlet of the shell side of process reboiler 116. An outlet of the shell side of process reboiler 116 is connected to an intermediate inlet of reboiler column 144 by a line 200.

Excess steam produced by the present process and not needed for steam stripping of the rich alkaline scrubbing agent may be directed to export via line 202. A representative material balance for the process carried out using the apparatus above schematically in FIG. 2, is shown in the box score of Example 2 hereinafter.

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the rich scrubbing solution is limited primarily by an acceptable temperature approach between the rich scrubbing solution and the lean scrubbing solution with a temperature approach of about 4-5° F. being a requisite for efficient operation. Best results are obtained when the temperature approach between the rich scrubbing solution and the lean scrubbing solution is maintained at a level of at least about 4-5° F. as in the example above.

In the instances of example given, where the low temperature shift effluent from a steam reforming reaction is treated in system 110, a process having parameters of the general values given in the example provides 50 psig steam which can be used to drive the steam jets of jet assembly 106 without the need for other auxiliary equipment. However, if desired and for other operating parameters, higher pressure steam driven jets may be used or compressors may be employed for this purpose.

It is also noteworthy that pure steam as stream S-13 is produced as the gaseous overhead from rich-reflux reboiler 138, and similarly that pure steam is produced as the overhead stream S-12 from rich-reflux reboiler 140, thus permitting introduction of this steam directly into heat load on the scrubbing solution 144. In the case of schemes where the scrubbing solution such as stream S-7 having regenerator column 144 are bled to produce steam, this not only limits the use of such steam because it contains some CO₂ when returned to the regenerator 144, but also causes additional vapor traffic in the regenerator column 144. In like manner, utilization of the reboilers 138 and 140 to produce steam while at the same time lowering the temperature of the rich scrubbing solution assists in minimizing the heat load on the stripper which can cause liquid distribution difficulties in the regenerator 144.

The improved results that are obtained with the present process are exemplified by the following comparison:

TABLE 3

Configuration	CO ₂ Removed (MMBTU/H)	Capacity 900 STD/NH ₃ plant (MMBTU/H)	CO ₂ Removed (MMBTU/H)	Capacity 900 STD/NH ₃ plant (MMBTU/H)
Conventional Rich-reflux (without vacuum)	94.00	11.90	0	n.a.
Rich-reflux (vacuum jet)	83.90	0	14.53	0
Rich-reflux (vacuum/steam)	69.40	0	21.60	0

NOTE: Export steam pressure is 50 psig.

As is also apparent from the exemplary example of Table 3 above, and assuming the parameters of that example, not only is adequate steam produced for full stripping of the rich scrubbing solution supplied to the regenerator column 44, but in addition, 14.53 pounds per hour of steam at a temperature of 298° F. and a pressure of 63 psig is available for export.

1. A process for removal of an acid gas from a gas-liquid mixture comprising the steps of: bringing the mixture into contact with a sufficient amount of a lean aqueous solution of an alkaline

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scrubbing agent under an elevated absorption pressure to produce a rich scrubbing solution and the rich scrubbing solution is then contacted with the acid gas to be scrubbed at a temperature of at least about 180° F. by virtue of the exothermic reaction between the acid gas and the alkaline agent;

regenerating the rich scrubbing solution at a regeneration pressure substantially less than said absorption pressure by subjecting the rich solution to sufficient stripping steam to remove acid gas therefrom so that the resulting lean scrubbing solution may be reused for acid gas absorption;

bringing the rich scrubbing solution at said temperature of at least about 180° F. into indirect heat exchange relationship with condensate at a lower temperature than the rich scrubbing solution, and a temperature above said regeneration pressure;

the temperature approach between the rich scrubbing solution and the condensate being maintained at a value no less than about 4-5° F.;

maintaining the rich scrubbing solution at heat exchange relationship with said condensate for a period sufficient to raise the temperature of the scrubbing solution and effect heating of at least a part of the condensate to a level to produce secondary steam;

collecting the secondary steam and adding such secondary steam to the stripping steam used for regeneration of the rich scrubbing solution;

2. A process as set forth in claim 1, wherein is included the steps of bringing the condensate which has been heated to produce secondary steam into further indirect heat exchange relationship with the rich scrubbing solution at a temperature above about 180° F. and adding said secondary steam to the stripping steam at a pressure above said regeneration pressure for a time period sufficient to effect additional heating of at least a part of the condensate to a level to produce tertiary steam;

3. A process as set forth in claim 1, wherein is included the step of decreasing the pressure on the condensate during production of tertiary steam therefrom to enhance the degree of tertiary steam production;

4. A process as set forth in claim 3, wherein said step of decreasing the pressure on the condensate is accomplished by communicating the condensate with the vacuum part of a steam jet while the steam jet is in indirect heat exchange relationship with the rich scrubbing solution;

5. A process as set forth in claim 3, wherein the steam exiting from the steam jet is combined with the tertiary steam and the secondary steam for use thereof to effect stripping of the rich scrubbing solution;

6. A process as set forth in claim 1, wherein is included the step of maintaining the temperature approach between the rich scrubbing solution and the condensate at a level of at least about 4-5° F.

7. A process as set forth in claim 1, wherein is included the steps of bringing the rich scrubbing solution at a temperature above about 240° F. into heat exchange relationship with the condensate, and maintaining the

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condensate at a temperature no greater than about 230° F. prior to the condensate being brought into indirect heat exchange relationship with the rich scrubbing solution.

8. A process as set forth in claim 1, wherein is included in the step of deriving said condensate by condensing at least part of the steam utilized to effect stripping of the rich scrubbing solution.

9. A process as set forth in claim 1 wherein said indirect heat exchange with the condensate with the rich scrubbing solution includes the steps of providing a rich-reflux reboiler, and introducing the rich scrubbing solution into the rich-reflux reboiler for said indirect heat exchange with the condensate.

10. A process as set forth in claim 9, wherein is included the step of providing a rich-lean reboiler, and further including the steps of directing the rich scrubbing solution and the condensate to the rich-reflux reboiler and the rich-lean reboiler in successive order.

11. A process as set forth in claim 9, wherein is included the step of imposing a vacuum condition on the condensate side of the rich-lean reboiler to enhance recovery of steam from the condensate.

12. A process as set forth in claim 11, wherein the acid gas-containing mixture which is brought into contact with the lean aqueous alkaline scrubbing agent contains a quantity of nitrogen, and wherein the step of imposing a vacuum condition on the rich-lean reboiler includes the step of providing a steam jet directing steam removed from the gas-liquid mixture into the steam jet, and the steam jet is in indirect heat exchange relationship with the rich-lean reboiler.

13. A process as set forth in claim 12, wherein is included the step of bringing the condensate from the rich-reflux reboiler into indirect heat exchange relationship with the rich scrubbing solution after the latter has been directed through the rich-reflux reboiler.

14. A process as set forth in claim 13, wherein is included the step of maintaining the temperature approach between the rich scrubbing solution and the condensate directed to the rich-lean reboiler at a level of at least about 4-5° F.

15. A process as set forth in claim 13, wherein is included the steps of bringing the rich scrubbing solution into the rich-lean reboiler at a temperature above about 240° F., and maintaining the condensate directed to the rich-lean reboiler at a temperature no greater than about 230° F.

16. In a process as set forth in claim 9, wherein is included the step of deriving the condensate by condensing at least a part of the steam used to effect stripping of the rich scrubbing solution.

17. A process for removal of an acid gas from a gas-liquid mixture comprising the steps of: bringing the mixture into contact with a sufficient amount of a lean aqueous solution of an alkaline scrubbing agent under an elevated absorption pressure to effect absorption of the acid gas by the agent therein and raise the temperature of the resulting rich scrubbing solution to a level of at least about 180° F. by virtue of the exothermic reaction between the acid gas and the alkaline agent;

regenerating the rich scrubbing solution at regeneration pressure substantially less than said absorption pressure by subjecting the rich solution to sufficient stripping steam to remove acid gas therefrom so that the resulting lean scrubbing solution may be reused for acid gas absorption;

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from so that the resulting lean scrubbing solution may be reused for acid gas absorption; bringing the rich scrubbing solution at said temperature of at least about 180° F. into indirect heat exchange relationship with condensate at a lower temperature than the rich scrubbing solution and at a pressure above said regeneration pressure; the temperature approach between the rich scrubbing solution and the condensate being maintained at a value no less than about 4-5° F.;

maintaining the rich scrubbing solution in heat exchange relationship with said condensate for a third period sufficient to lower the temperature of the scrubbing solution and effect heating of at least a part of the condensate to a level to produce secondary steam; and

collecting the secondary steam and expiring such steam to a remote point for use thereof;

19. Apparatus for removing an acid gas from a gas-liquid mixture comprising the steps of: bringing the mixture into contact with a lean aqueous solution of an alkaline scrubbing agent under an elevated absorption pressure to effect absorption of the acid gas by the agent therein and raise the temperature of the resulting rich scrubbing solution to a level of at least about 180° F. by virtue of the exothermic reaction between the acid gas and the alkaline agent;

means for regenerating the rich scrubbing solution to a lean condition by steam stripping for reuse of the solution;

means for recovering heat of reaction derived therefrom energy from the rich scrubbing solution to produce steam for use as at least a part of the steam required to steam strip the rich scrubbing solution to remove absorbed acid gas therefrom, said heat recovery means including a rich-reflux reboiler;

means for directing condensate into the rich-reflux reboiler;

means for introducing the rich scrubbing solution at a temperature above about 180° F. and at a pressure above said regeneration pressure into the rich-reflux reboiler for indirect heat exchange with the condensate supplied thereto at a lower temperature than the rich scrubbing solution;

the temperature approach between the rich scrubbing solution and the condensate being maintained at a value no less than about 4-5° F.;

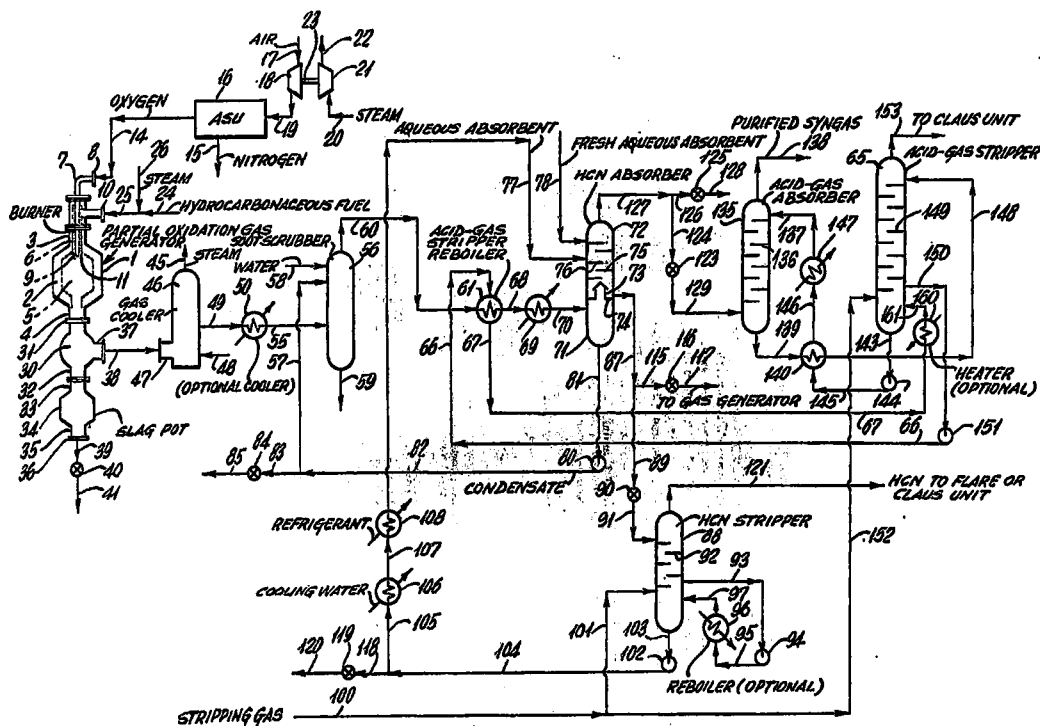
means for maintaining the rich scrubbing solution in indirect heat exchange relationship with the condensate in said rich-reflux reboiler at a pressure above said regeneration pressure and for a period sufficient to lower the temperature of the scrubbing solution and effect heating of at least a part of the condensate to produce secondary steam;

and for recovering secondary steam from the rich-reflux reboiler; and

means for conveying at least a portion of the secondary steam recovered from the rich-reflux reboiler to the regenerator to effect steam stripping of the rich scrubbing solution delivered thereto.

20. Apparatus as set forth in claim 18, wherein is provided a rich-lean reboiler, and means for directing the rich scrubbing solution and the condensate to the rich-reflux reboiler and the rich-lean reboiler in successive

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PRODUCTION OF CLEAN HCN-FREE SYNTHESIS GAS

BACKGROUND OF THE INVENTION

1. Field of the invention
This invention relates to a continuous partial oxidation process for the production of a stream of clean synthesis gas that is substantially free from HCN. If present, other acid gases may be separately removed.
2. Description of the prior art
Three amounts of HCN, i.e., 0.3 to 100 parts per million (ppm) by weight in the synthesis gas, are sufficient to deactivate the catalysts for (a) or (b) synthesis gas, as is known in the art. HCN is a toxic gas and is also a poison for (a) or (b) synthesis gas. HCN is a gas stream may corrode acid stripping and scrubbers. Further, the life of some liquid organic absorbents that are employed in conventional downstream acid-gas removal systems may be shortened by the presence of HCN impurities in the gas stream. HCN may be removed from synthesis gas when the gas stream is subjected to the catalytic water gas shift reaction. However, this step will change the H₂/CO molar ratio of the gas stream and, produces unwanted nitrogen oxides and ammonia. Advantageously, by the subject process, substantially all of the HCN is removed from synthesis gas without changing the H₂/CO of the molar ratio of the product gas. Further, the HCN is disposed of without polluting the environment.

SUMMARY

This is a continuous partial oxidation process for producing clean synthesis gas that is substantially free from HCN. The amount of HCN in the product gas will have been reduced to less than 0.3 parts per million. In the process, raw synthesis gas, i.e., gaseous mixtures comprising H₂+CO, containing about 0.3 to 100 ppm of HCN is produced by the partial oxidation of hydrocarbonaceous feed in a free-flow monolithically synthesis gas generator. The gas stream is then subjected to a series of steps to remove HCN. First, the gas stream is partially cooled and is then contacted with a liquid organic absorbent in a gas scrubber. The scrubbing zone below the dew point in a gas cooling zone. In one embodiment, the hydrocarbonaceous feed contains sulfur, impurities and acid gases from the group H₂S, COS and CO₂ which are removed downstream in an acid-gas purification zone. In such cases, the rich liquid organic absorbent from the acid-gas purification operation may be heated and regenerated by indirect heat exchange with the clean gas stream in a solid gas cooling zone. Each million Standard Cubic Feet (SCF) of clean synthesis gas is then contacted with about 200 to 500 gallons (gals.) say 250-350 gals. of cold aqueous absorbent at a temperature in the range of about 35° to 120° F., preferably below 100° F., say 50° to 95° F., and a pressure in the range of about 5 to 3000 psia, preferably at least 100 psia, say 100 to 1000 psia. A clean stream of synthesis gas, substantially free from HCN, is removed from the top of the absorption column, and is optionally subjected to further purification in an acid-gas purification operation to remove any acid gases that may be present, as previously mentioned. The HCN-rich aqueous absorbent may be regenerated by heating, stripping, or both in a stripping column. The overhead gas stream from the HCN-stripping column may be recycled to the gas generator or introduced into a sulfur-recovery operation, or discharged to flare. Altern-

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tively, at least a portion of the HCN-rich aqueous absorbent may be introduced into the gas generator in liquid or vapor phase. By the subject process, environmental pollution is avoided.

BRIEF DESCRIPTION OF THE DRAWING

The invention will be further understood by reference to the accompanying drawing. The drawing is a preferred embodiment of the process for producing a clean stream of synthesis gas containing substantially no HCN. Further, there is depicted the separate removal of at least one gaseous impurity from the group H₂S, COS, and CO₂ when present in the stream of raw synthesis gas.

DESCRIPTION OF THE INVENTION

The present invention pertains to an improved continuous partial oxidation process for producing a stream of synthesis gas that is substantially free from HCN. By definition, the term "substantially free" means from 0 to 0.3 Parts Per Million (PPM) (by weight dry basis). By means of the subject process, the lives of the catalysts that are contacted by the improved HCN-free synthesis gas may be extended at a great economic benefit. For example, in one catalytic oxo-synthesis operation, it was estimated that a savings of 7 million dollars a year in catalyst costs alone could be effected by removing the trace amounts of HCN from the synthesis gas feed stream.

Removal of H₂S and COS when present, by optional additional steps, is also beneficial for extending the life of sulfur-sensitive catalysts.

Optional steps are provided for removing acid gases such as H₂S, COS and CO₂ if present in the HCN-free synthesis gas. Further, the subject process provides for the safe disposal of the HCN as well as any other acid gas impurities that are removed by the subject process, without polluting the atmosphere.

In the subject process, a hydrocarbonaceous feed is reacted with a free-oxygen containing gas, optionally with or without a temperature moderator, in the reaction zone of a free-flow monolithically synthesis gas generator at a temperature in the range of about 1300° to 3500° F., say about 1800° to 2800° F., and a pressure in the range of about 1 to 250 atmospheres absolute (atm. abs.), say about 10 to 200 atm. abs. or 40 to 100 atm. abs. The reaction time in the gas generator is about 1 to 10 seconds. The effluent stream of raw synthesis gas leaving the gas generator comprises H₂, CO, CO₂, HCN and at least one material from the group H₂O, H₂S, COS, CH₄, N₂, Ar, NH₃ and entrained particulate solids. The composition of the raw synthesis gas in mole % may be as follows: H₂ 10.0 to 64.0, CO 15.0 to 60.0, CO₂ 5.0 to 30.0, H₂O 2.0 to 50.0, CH₄ 0 to 20.0, H₂S 0.0 to 5.0, COS 0.0 to 0.3, N₂ 0.0 to 60.0, Ar 0.0 to 1.0, and NH₃ 0 to 0.2. HCN is present in the amount of about 0.3 to 100 ppm (weight basis). Unreacted particulate carbon (on the basis of carbon in the feed by weight) is present in the amount of about 0.2 to 20 weight percent with liquid feeds and is usually negligible with gaseous hydrocarbon feeds.

A free-flow synthesis gas generator comprising a vertical cylindrical shaped steel pressure vessel lined with refractory, such as shown in the drawing is used. The gas generator is free from packing or catalyst. The feed streams are introduced into the reaction zone of the feed gas generator by means of a fuel burner. Suitably,

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7 is an excellent scrubbing fluid because of its lower molecular weight, greater density, and lower cost in comparison with organic solvents. Dilute solutions of water and sulfuric acid i.e. up to 10 vol. % H_2SO_4 and dilute water solutions i.e. up to saturated solutions of the carbonates, bicarbonates, and mixtures thereof of an element or mixture of elements selected from Group IA elements i.e. Na, K, Li, and mixtures thereof, also fall within the definition of "aqueous absorbent". For example, an aqueous solution in the range of about 1 to 10 wt. % sodium carbonate, potassium carbonate, lithium carbonate, and mixtures thereof may be used as the "aqueous absorbent". Dilute sulfuric acid is particularly effective for HCN absorption as it shifts the equilibrium of the reaction $HCN + H_2O \rightleftharpoons HCNH_2 + OH^-$ to the right. The rate of HCN absorption is also enhanced by physical expanding means i.e. bubbling, spraying, or both. Regeneration of the rich absorbent, on the other hand, is effected by chemical treatment to remove the cyanide. For example, by heating the rich absorbent to a temperature in the range of about 430° F. to 500° F. for about one hr. under autogenic pressure, sodium or potassium cyanide may be hydrolyzed to ammonia and sodium or potassium formate. The CO_2 in synthesis gas reacts with the sodium or potassium formate to produce sodium or potassium carbonate-bicarbonate. Optionally, at least a portion of the rich-dilute-alkali absorbent from the HCN absorber may be introduced into the gas generator.

Each million standard cubic feet (SCF) of clean de-watered synthesis gas is contacted with about 200 to 300 gallons, say 250 to 350 gallons of aqueous absorbent in liquid phase in the HCN absorption column. The HCN-rich aqueous absorbent containing up to about 500 ppm HCN is removed from the bottom chimney tray in the HCN absorber column. It is then processed in the HCN stripper to remove the dissolved HCN, and then cooled and recycled to the HCN-absorption column to contact additional synthesis gas. Alternatively, at least a portion of the HCN-rich aqueous absorbent may be safely disposed of by being introduced into the gas generator in liquid or vapor phase at least a portion of the temperature of the HCN absorber, or externally thereof, the HCN may be fed with H_2O to produce a feed emulsion in which water or a dilute aqueous solution of sulfuric acid is employed as the aqueous absorbent, the regeneration of the HCN-rich aqueous absorbent may be effected by the physical means of a gas stripping operation by which the gaseous HCN is separated from the aqueous absorbent. For example, in a conventional multi-plate stripping column, with or without a reboiler, the HCN-rich aqueous absorbent at a temperature in the range of about 50° F. to 120° F. and at reduced pressure i.e. a pressure in the range of about 1 to 2 atmospheres gauge, is introduced near the top of the column and HCN-free aqueous absorbent is removed from the bottom. Optionally, stripping gas, such as nitrogen or steam may be introduced near the bottom of the HCN absorber. The gaseous HCN stream leaving near the top of the HCN absorber may be disposed of by any of the following ways: sent to flare, burned in a furnace or in the gas generator, or sent to a Claus operation. The HCN-free reclaimed aqueous absorbent, containing less than 1.5 parts per million of HCN leaves at the bottom of the HCN-stripper at a temperature in the range of about 130° F. to 300° F. It is then pumped through a cooling zone where

described process in detail. All of the lines and equipment are preferably insulated to minimize heat loss. Referring to the lines in the drawing, free-flow non-catalytic gas from the gas generator 1 lined with refractory 2 previously described has an upstream initially flanged inlet port 3, a downstream initially flanged outlet port 4, and an unpigged side stream 5. Ammonia type burner 6, as previously described, has center passage 7 in alignment with the axis of gas generator 1 is mounted in inlet port 3. Center passage 7 has a flanged up-stream inlet 8 and a converging conical shaped downstream nozzle 9 at the tip of the burner. Burner 6 is also provided with a concentric coaxial annular passage that has an upstream flanged inlet 10 and a downstream conical shaped discharge passage 11. Burners of other design may also be used. A continuous stream of free-oxygen containing gas i.e. substantially pure oxygen is passed through line 14 into flanged inlet 8 of burner 6.

The oxygen in line 14 and nitrogen in line 15 are produced in a conventional air separation unit 16. Air from line 17 is compressed by compressor 18 and passed through line 19 into air separation unit (ASU) 16. A portion of the stream from line 43 of gas cooler 46 is passed through line 20 of expansion turbine 21 as the working fluid. Spent steam leaves by way of line 22. Shaft 23 of turbine 21 is coupled to and drives compressor 18. A hydrocarbonaceous feed is introduced into burner 6 by way of lines 24, 25, and inlet 10. Optionally, steam in line 26 may be used to atomize the hydrocarbonaceous fuel.

Refractory lined or insulated flanged "T" connector 30 may be suitably spherically shaped and is joined to inlet 31 to outlet 4 of gas generator 1. A line 32 is connected to inlet 31 of line 33 and slag pot 34. Slagged acid outlet 35 is normally in the closed position by closing valve 41. Steam from gas generator 1 passes through line 36, then enters connector 30 through inlet 31 and leaves through outlet 37 and insulated line 38. Depending on the composition of the hydrocarbonaceous fuel, particulate solids i.e. slag, carbon, metals, or refractory may leave through outlet 4. At least a portion of the solid material may separate from the effluent gas stream in connector 30 and accumulate in the bottom of slag pot 34. Any material in slag pot 34 is periodically removed through line 39, valve 40, line 41 or through a conventional lock-hopper system not shown. The temperature and pressure of the raw gas stream passing through connector 30, outlet 37 and line 38 is substantially unaffected since the lines are insulated and unobstructed.

The hot effluent stream of generator gas in line 38 is introduced into gas cooler 46 by way of inlet 47. The hot gas stream is cooled by passing in indirect heat exchange with boiler feed water which enters gas cooler 46 through line 48 and which leaves as steam through line 49. Optionally, additional heat may be extracted from the gas stream leaving gas cooler 46 through line 49 by means of heat exchanger or condenser 50. For example, the oxygen stream in line 14 may be preheated in economizer 50 prior to being introduced into burner 6.

The cooled gas stream in line 51 is passed into acid scrubber 56 where it is contacted with a counter-flow stream of water e.g. condensate, from line 57. The gas stream leaving scrubber 56 is given a final rinse with fresh make-up water from line 58. A dispersion of

water and particulate carbon is removed through line 59 and is sent to a conventional carbon recovery zone (not shown). Particulate carbon is recovered in the carbon recovery zone and recycled to the gas generator as a portion of the fuel. Thus, substantially all of the carbon in the fuel is eventually gasified and the efficiency of the process is improved.

The clean gas stream leaving scrubber 56 is passed through line 60 into heat exchanger or reboiler 61. The clean gas stream is thereby cooled by indirect heat exchange with liquid absorbent from acid gas stripper 63 located downstream in the process. The liquid absorbent enters reboiler 61 through line 66. After being heated therein, for example to the boiling point, the acid gas stripper 63. Optionally, further cooling of the gas stream in line 68 may be effected by passing the gas stream through heat exchanger or cooler 69 in indirect heat exchange with a coolant, such as cold water. By this means the gas stream is cooled below the dew point and water is separated.

The cooled clean stream of synthesis gas in line 70 is then introduced into the lower chamber 71 of HCN absorber 72, where the condensed water is collected. The de-watered gas stream passes up through reboiler 73 in bottom chimney tray 74. It then passes up through a plurality of trays 75 in upper section 76 of absorber 72 while in direct contact with cold make-up absorbent which enters through line 77 and then passes down through column 72. The gas stream leaving the column may be given a final rinse with cold make-up absorbent as in a conventional plate column with a plurality of trays 76 for liquid-gas contacting, or alternatively a conventional packed column.

At least a portion of condensate in bottom chamber 71 is pumped by means of pump 80 through lines 81, 82 and 57 into scrubber 56. Optionally, a portion of the condensate may be passed through line 83, valve 84, line 85, and introduced into gas generator 1, discarded from the system. Alternatively before recycle to scrubber 56, the condensate in line 82 may be degassed, for example in a pressure reduction operation (not shown). The gases released may be sent to flare or to a Claus unit. The HCN-rich aqueous absorbent leaves HCN absorber 72 and is preferably introduced into HCN stripper 88 by way of lines 87, 89, expansion valve 90, and line 91. Stripper 88 is a conventional gas-liquid desorption column with a plurality of plates 92. Aqueous absorbent is optionally, removed through line 93 and pumped by means of pump 94 through line 95 into reboiler 96. After being heated the aqueous absorbent is returned to stripper 88 by way of line 97. Optionally stripping gas in line 100 is passed through line 101 into the bottom of stripper 88. By means of pump 102, the lean aqueous absorbent is pumped through lines 103 to 105, cooled in heat exchanger 106 with cooling water, line 107, cooled in heat exchanger 108 with refrigerant, and line 109, at least a portion of the rich aqueous absorbent in line 97 may be passed through line 115, valve 116, and line 117 and disposed of in gas generator 1 as a portion of the feed stream. Alternatively, the absorbent stream may be sent to a Claus operation. The HCN to ammonia is 700° F. in order to hydrolyze the HCN to ammonia and carbon monoxide before it is mixed with the hydrocarbonaceous fuel and introduced into gas generator 1.

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such as benzene, toluene, xylene, and coal tar, cyclohexane, and mixtures thereof, in a liquid carrier such as water, liquid hydrocarbon, and mixtures thereof.

8. The process of claim 1 in which the aqueous absorbent in step (5) is a dilute solution of water containing up to 10 volume % sulfuric acid.

9. The process of claim 1 in which the aqueous absorbent in step (5) is a dilute water solution of the carbonates, bicarbonates, and mixtures thereof of an element or mixture of elements selected from Group 1A elements.

10. The process of claim 1 in which said stream of acid gas is introduced into said recovery operation for the production of sulfur.

11. The process of claim 9 with the added step of removing rich-dilute absorbent from the HCN absorber.

12. The process of claim 1 with the added step of chemical treatment, and recycling the regenerated absorbent to the HCN absorber.

13. The process of claim 1 with the added step of degassing the condensed water from step (4) before recycling said condensate to the gas scrubbing zone in step (3).

14. The process of claim 1 with the added step of introducing a portion of the condensed water from step (4) into the gas generator.

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such as benzene, toluene, xylene, and coal tar, cyclohexane, and mixtures thereof, in a liquid carrier such as water, liquid hydrocarbon, and mixtures thereof.

4. The process of claim 1 in which said hydrocarbonaceous fuel is a mixture of gaseous hydrocarbons.

5. The process of claim 1 in which said hydrocarbonaceous fuel is an oxygenated hydrocarbonaceous organic material selected from the group consisting of carboxylic acids, alcohols, ketones, aldehydes, organic acids, alcohols, ketones, oxygenated fuel oil, waste liquids and by-products from chemical processes containing oxygenated hydrocarbonaceous organic materials, and mixtures thereof.

6. The process of claim 1 provided with the step of removing at least a portion of unwanted solid matter from the group particulate carbon, ash, slag, scale, refinery, and mixtures thereof contained in the gas stream leaving the gas generator or flowing from the gas generator, before introducing said gas stream into said cooling zone in step (2).

7. The process of claim 1 in which said hydrocarbonaceous fuel is a pumpable slurry of solid carbonaceous material selected from the group consisting of coal, lignite, particulate carbon, petroleum coke concentrated lower

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and at least one material from the group H_2O , H_2S , CO_2 , CH_4 , N_2 , A , and NH_3 .

(2) removing at least a portion of said entrained solids and cooling the gas stream to a temperature in the range of about $300^\circ F.$ to $900^\circ F.$

(3) cleaning the gas stream from (2) in a gas-scrubbing zone by scrubbing with condensate and make-up water if any so as to remove the remaining entrained solids without removing substantial amounts of HCN and to produce a clean synthesis gas stream containing HCN as an impurity.

(4) cooling the gas stream in the range of about $212^\circ F.$ to $600^\circ F.$ and at a pressure which is substantially the same as that in the synthesis gas generator less ordinary pressure drop in the intervening lines and equipment;

(5) separating water from said gas stream and recycling at least a portion of the condensed water to the gas scrubbing zone in (3) as said condensate;

(6) introducing the clean gas stream from (5) containing HCN impurity into an HCN-absorption zone and contacting said gas stream therein with an aqueous absorbent comprising about 90 to 100 volume % of about $50^\circ F.$ to $95^\circ F.$ and a pressure in the range of about 100 to 1600 psia so as to produce an HCN-rich aqueous absorbent stream;

(7) removing clean substantially HCN-free synthesis gas from said HCN-absorption zone; and introducing at least a portion of the HCN-rich aqueous absorbent stream from (7) into said gas generator in (1);

(8) introducing the remainder of said HCN-rich aqueous absorbent stream into an HCN-stripping zone at reduced pressure with or without reboiling and separately removing therefrom a stream of gaseous impurities and a lean aqueous absorbent stream; and introducing said gaseous stream of impurities into the synthesis gas generator in (1) or into a Claus operation or sending same to flare;

(9) cooling said lean aqueous absorbent from (7) and recycling same to the HCN-absorption zone in (7);

(10) contacting the clean substantially HCN-free synthesis gas from (7) with lean liquid absorbent in an acid-gas absorption zone and separately removing a stream of rich liquid absorbent and said product gas; and

(11) treating the stream of rich liquid absorbent from (10) and regenerating same in a regeneration zone wherein at least a portion of said liquid absorbent is heated during regeneration by indirect heat exchange with the clean gas stream leaving the scrubbing zone in (3); cooling the lean liquid absorbent from said regeneration zone and recycling same to said acid-gas absorption zone; and removing from said regeneration zone a stream of acid gas.

2. The process of claim 1 in which the free-oxygen-containing gas is selected from the group consisting of air, oxygen-enriched air (more than 21 mole % O_2), and substantially pure oxygen (more than 95 mole % O_2).

3. The process of claim 1 in which said hydrocarbonaceous fuel is a liquid hydrocarbon selected from the group consisting of liquefied petroleum gas, petroleum distillates and residues, gasoline, naphtha, kerosene, crude petroleum, asphalt, gas oil, residual oil, tar-sand oil, shale oil, coal derived oil, aromatic hydrocarbons

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Similarly, if desired a portion of the lean aqueous absorbent in line 104 may be passed through line 118, valve 119, and line 120 into line 121 disposed of by partial oxidation in gas generator 1 as a portion of the temperature moderating stream of gas from HCN

stripper 88 in line 121 principally comprises HCN and optionally stripping gas such as nitrogen. There may also be present a small amount less than 10 volume % of CO_2 , H_2S , and NH_3 .

This gas stream may be sent to flare, or to a Claus Unit or be used in a furnace.

With valve 123 in line 124 closed, and valve 125 in line 126 open, the clean HCN-free synthesis gas leaves from the top of HCN absorber 72 by way of lines 127, 128, and 129. Should acid gases be present which require removal, then valve 125 is closed, valve 123 is opened, and the HCN-free gas stream in line 127 is passed through lines 124, and 129 into the bottom of acid gas absorption column 135. Acid gas absorber 135 is a conventional gas-liquid absorption column containing a plurality of plates 136. The HCN-free gas stream enters up through the column comes directly into contact with the lean liquid organic absorbent which enters through line 137 and flows down through the column. Purified synthesis gas free from HCN and acid gases leaves through line 138 at the top of acid gas absorber 135.

Rich liquid organic absorbent leaves through line 139 at the bottom of acid gas absorber 135 and is heated in heat exchanger 140 by indirect heat exchange with lean liquid organic absorbent from line 145. Further cooling of the lean liquid organic absorbent in line 146 is effected in heat exchanger 147 by indirect heat exchange with cold water. The heated rich liquid organic absorbent is passed through line 148 and into the upper portion of acid gas stripper 65 where it flows down the column and is regenerated. Acid gas stripper 65 is a conventional gas-liquid absorption column containing a plurality of plates 149. A stream of partially desorbed liquid organic absorbent material is removed through line 150 near the bottom of column 65 and by means of pump 151 is passed through line 66, and reboiler 61. The heated liquid organic absorbent is introduced into column 65 near the bottom by way of line 67, optional heater 160, and line 161. Optionally, nitrogen stripping gas is passed through lines 160, 162, and is introduced into column 65 near the bottom. The overhead stream of gaseous impurities leaves acid gas stripper 65 through line 163 and is introduced into a Claus unit or sent to flare.

Obviously many modifications and variations of the invention as heretofore set forth may be made without departing from the spirit and scope thereof, and only such limitations should be composed as are indicated in the appended claims.

I claim:

1. A process for producing a clean stream of synthesis gas containing substantially no HCN nor sulfur-containing gases comprising:

(1) contacting a hydrocarbonaceous feed by partial oxidation with a free-oxygen-containing gas with or without a temperature moderating stream in the reaction zone of a free-flow synthesis gas generator at a temperature in the range of about $1300^\circ F.$ to $3500^\circ F.$ and at a pressure in the range of about 10 to 200 atmospheres to produce a stream of synthesis gas comprising H_2 , CO , CO_2 , HCN, entrained solids

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such as benzene, toluene, xylene, and coal tar, cyclohexane, and mixtures thereof, in a liquid carrier such as water, liquid hydrocarbon, and mixtures thereof.

4. The process of claim 1 in which said hydrocarbonaceous fuel is a mixture of gaseous hydrocarbons.

5. The process of claim 1 in which said hydrocarbonaceous fuel is an oxygenated hydrocarbonaceous organic material selected from the group consisting of carboxylic acids, alcohols, ketones, aldehydes, organic acids, alcohols, ketones, oxygenated fuel oil, waste liquids and by-products from chemical processes containing oxygenated hydrocarbonaceous organic materials, and mixtures thereof.

6. The process of claim 1 provided with the step of removing at least a portion of unwanted solid matter from the group particulate carbon, ash, slag, scale, refinery, and mixtures thereof contained in the gas stream leaving the gas generator or flowing from the gas generator, before introducing said gas stream into said cooling zone in step (2).

7. The process of claim 1 in which said hydrocarbonaceous fuel is a pumpable slurry of solid carbonaceous material selected from the group consisting of coal, lignite, particulate carbon, petroleum coke concentrated lower

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and at least one material from the group H_2O , H_2S , CO_2 , CH_4 , N_2 , A , and NH_3 .

(2) removing at least a portion of said entrained solids and cooling the gas stream to a temperature in the range of about $300^\circ F.$ to $900^\circ F.$

(3) cleaning the gas stream from (2) in a gas-scrubbing zone by scrubbing with condensate and make-up water if any so as to remove the remaining entrained solids without removing substantial amounts of HCN and to produce a clean synthesis gas stream containing HCN as an impurity.

(4) cooling the gas stream in the range of about $212^\circ F.$ to $600^\circ F.$ and at a pressure which is substantially the same as that in the synthesis gas generator less ordinary pressure drop in the intervening lines and equipment;

(5) separating water from said gas stream and recycling at least a portion of the condensed water to the gas scrubbing zone in (3) as said condensate;

(6) introducing the clean gas stream from (5) containing HCN impurity into an HCN-absorption zone and contacting said gas stream therein with an aqueous absorbent comprising about 90 to 100 volume % of about $50^\circ F.$ to $95^\circ F.$ and a pressure in the range of about 100 to 1600 psia so as to produce an HCN-rich aqueous absorbent stream;

(7) removing clean substantially HCN-free synthesis gas from said HCN-absorption zone; and introducing at least a portion of the HCN-rich aqueous absorbent stream from (7) into said gas generator in (1);

(8) introducing the remainder of said HCN-rich aqueous absorbent stream into an HCN-stripping zone at reduced pressure with or without reboiling and separately removing therefrom a stream of gaseous impurities and a lean aqueous absorbent stream; and introducing said gaseous stream of impurities into the synthesis gas generator in (1) or into a Claus operation or sending same to flare;

(9) cooling said lean aqueous absorbent from (7) and recycling same to the HCN-absorption zone in (7);

(10) contacting the clean substantially HCN-free synthesis gas from (7) with lean liquid absorbent in an acid-gas absorption zone and separately removing a stream of rich liquid absorbent and said product gas; and

(11) treating the stream of rich liquid absorbent from (10) and regenerating same in a regeneration zone wherein at least a portion of said liquid absorbent is heated during regeneration by indirect heat exchange with the clean gas stream leaving the scrubbing zone in (3); cooling the lean liquid absorbent from said regeneration zone and recycling same to said acid-gas absorption zone; and removing from said regeneration zone a stream of acid gas.

2. The process of claim 1 in which the free-oxygen-containing gas is selected from the group consisting of air, oxygen-enriched air (more than 21 mole % O_2), and substantially pure oxygen (more than 95 mole % O_2).

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Similarly, if desired a portion of the lean aqueous absorbent in line 104 may be passed through line 118, valve 119, and line 120 into line 121 disposed of by partial oxidation in gas generator 1 as a portion of the temperature moderating stream of gas from HCN

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Rich liquid organic absorbent leaves through line 139 at the bottom of acid gas absorber 135 and is heated in heat exchanger 140 by indirect heat exchange with lean liquid organic absorbent from line 145. Further cooling of the lean liquid organic absorbent in line 146 is effected in heat exchanger 147 by indirect heat exchange with cold water. The heated rich liquid organic absorbent is passed through line 148 and into the upper portion of acid gas stripper 65 where it flows down the column and is regenerated. Acid gas stripper 65 is a conventional gas-liquid absorption column containing a plurality of plates 149. A stream of partially desorbed liquid organic absorbent material is removed through line 150 near the bottom of column 65 and by means of pump 151 is passed through line 66, and reboiler 61. The heated liquid organic absorbent is introduced into column 65 near the bottom by way of line 67, optional heater 160, and line 161. Optionally, nitrogen stripping gas is passed through lines 160, 162, and is introduced into column 65 near the bottom. The overhead stream of gaseous impurities leaves acid gas stripper 65 through line 163 and is introduced into a Claus unit or sent to flare.

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I claim:

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(1) contacting a hydrocarbonaceous feed by partial oxidation with a free-oxygen-containing gas with or without a temperature moderating stream in the reaction zone of a free-flow synthesis gas generator at a temperature in the range of about $1300^\circ F.$ to $3500^\circ F.$ and at a pressure in the range of about 10 to 200 atmospheres to produce a stream of synthesis gas comprising H_2 , CO , CO_2 , HCN, entrained solids