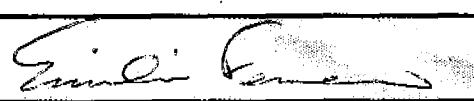




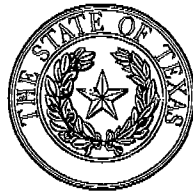
No. 06-101820-00005-0000

Fecha 2009-08-31 16:42:05 Dep. 2020 NULCREACIONI
Tra 11 PATENTEIYII Eve: 379 FASENACIONALII
Act. 329 CTOINFORMACION Folios: 10

FORMULARIO UNICO DE CORRECCIONES Y MODIFICACIONES

1	SOLICITUD DE: ☐ Corrección de Error Material ☒ Modificación a una solicitud	
2	SOLICITANTE Nombre: MARATHON GTF TECHNOLOGY, LTD. Sociedad constituida y existente bajo las leyes del Estado de Delaware, Estados Unidos de América. Dirección: 5555 San Felipe, Houston, Texas 77056-2799, Estados Unidos de América Domicilio: Houston, Texas 77056-2799, Estados Unidos de América Teléfono: 546 09 70 Fax: 249 40 70 E-mail: clientes@cavelier.com	IDENTIFICACION C.C. ☐ NIT ☐ C.E. ☐ Otro ☐ Número: _____
3	REPRESENTANTE O APODERADO Nombre: Emilio FERRERO Dirección: Carrera 4ª No. 72-35 Teléfono: 347 36 11 Fax: 217 92 11 E-mail: cavelier@cavelier.com	IDENTIFICACION C.C. ☒ NIT ☐ C.E. ☐ Otro ☐ Número: 438.019 TP 31.929
4	Número de expediente: <u>06.101.820</u>	
5	Descripción de la corrección o modificación solicitada: Atentamente informo a Su Despacho que la solicitud de la referencia ha sido cedida de la sociedad MARATHON OIL COMPANY en favor de la sociedad MARATHON GTF TECHNOLOGY, LTD.	
6	Comprobante de pago No. <u>09-57.048</u> Fecha: <u>3 de agosto de 2009</u>	
7	Anexos ☒ Comprobante de pago de la tasa por \$111.000, por concepto de modificaciones. ☒ Documento que acredita la cesión de la sociedad MARATHON OIL COMPANY en favor de la sociedad MARATHON GTF TECHNOLOGY, LTD. ☒ Poder de la sociedad MARATHON GTF TECHNOLOGY, LTD. ☒ Documento que acredita la existencia y representación legal de la la sociedad MARATHON GTF TECHNOLOGY, LTD.	
8	NOMBRE: EMILIO FERRERO	FIRMA:  C.C. 438.019. de Usaquén T.P.A. 31.929

SCT
COLO-00729-841-001-5
COLO-17154-843-001-5



1999 198

The State of Texas
Secretary of State

Not for use within the United States of America.

This Apostille only certifies the signature, the capacity of the signer and the seal or stamp it bears.
It does not certify the content of the document for which it was issued.

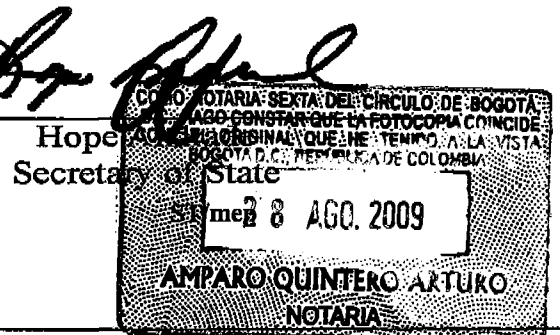
APOSTILLE

(Convention de La Haye du 5 Octobre 1961)

- | | |
|--------------------------------|--|
| 1. Country: | United States of America |
| This public document | |
| 2. has been signed by | HOLLY KEISER |
| 3. acting in the capacity of | Notary Public, State of Texas |
| 4. and bears the seal/stamp of | HOLLY KEISER, Notary Public, State of
Texas, Commission Expires: 04-17-11 |

CERTIFIED

- | | |
|---------------------------------------|----------------------|
| 5. at Austin, Texas | 6. on April 24, 2009 |
| 7. by the Secretary of State of Texas | |
| 8. Certificate No. N-694669 | |
| 9. Seal | 10. Signature: |



199
200

Documento de Traspaso, Representación y Poder con autenticación notarial y Apostille para patentes, modelos de utilidad, diseños industriales, marcas de fábrica, nombres comerciales, enseññas, nombres de dominio, lemas comerciales registradas o pendientes de registro, licencias.

Assignment with Representation and Power- of- Attorney with notarial authentication and Apostille for granted or pending patents, utility models, industrial designs, trademarks, commercial names, trade emblems, domain names, slogans, licenses.

DOCUMENTO DE TRASPASO, REPRESENTACION Y PODER

ASSIGNMENT WITH REPRESENTATION AND POWER OF ATTORNEY

Yo, (nosotros), abajo firmado (s) _____

domiciliado (s) en _____
aquí llamado (s) CEDENTE(s), propietario(s) de la(s) _____
_____(s) en _____
como sigue: _____

declara(n) por el presente instrumento que cede(n) la(s) dicha (s) _____
a _____
sociedad organizada y existente bajo las leyes de _____
domiciliada en _____

(aquí llamada la CESIONARIA). Por el presente acto, la CESIONARIA acepta dicho traspaso y nombra a LUZ CLEMENCIA DE PAEZ tpa. 23555, DANIEL PEÑA tpa N° 65.620, y GERMAN MARIN, tpa 64.239, domiciliados en la Carrera 4ª N° 72-35, Bogotá, Colombia, en obediencia a lo dispuesto en el parágrafo 1o del Artículo 543 del Código de Comercio, el primero como principal y los demás como suplentes, en su orden, como mis (nuestros) representantes en todos los asuntos de propiedad industrial con facultad para recibir notificaciones y nombrar apoderados judiciales o extrajudiciales. El primer representante suplente reemplazará al principal en caso de ausencia o impedimento temporal o definitivo de aquél. La misma regla se aplicará cuando el segundo representante suplente haya de reemplazar al primero, o el tercero al segundo. En tales casos, el representante principal, o el primero, o segundo suplente, en su caso, o ambos, declararán su intención de no ejercer la representación mediante declaración autenticada por Notario Público en Colombia, o por Notario u otro Funcionario Público, o Cónsul de Colombia, en el extranjero; y si se tratare de impedimento, con el certificado respectivo. Si alguno de los nombrados faltare definitivamente, el siguiente tomará su lugar. Cuando cesare la ausencia o impedimento del representante principal, o de su primero o segundo suplentes, en su caso, podrán ejercer la

I (we), the undersigned
MARATHON OIL COMPANY
Of
5555 San Felipe, Houston, Texas 77056-2799, United States of America

hereinafter the ASSIGNOR(s) owner of the
patent applications Nos. 06101820 and 08039674
in Colombia as follows:
PROCESS FOR CONVERTING GASEOUS ALKANES TO LIQUID
HYDROCARBONS and
PROCESS FOR CONVERTING GASEOUS ALKANES TO OLEFINS
AND LIQUID HYDROCARBONS

declares by this document that assigns the mentioned
patent applications
to
MARATHON GTF TECHNOLOGY, LTD.
a corporation organized and existent under the laws of
State of Delaware, United States of America
and domiciled in
5555 San Felipe, Houston, Texas 77056-2799, United States of America

which in this document will be called the ASSIGNEE). The ASSIGNEE accepts the said assignment and in due compliance with the terms of paragraph 1st. of article 543 of the Commercial Code, do hereby appoint LUZ CLEMENCIA DE PAEZ tpa. 23555, DANIEL PEÑA tpa N° 65.620, y GERMAN MARIN tpa 64.239, domiciled at Carrera 4ª N° 72-35, Bogotá, Colombia, the first as principal and the others as alternates, in the order of their appointment, as our representatives for all industrial property matters with faculty to receive notifications and to appoint attorneys in and out of Court. The first alternate shall replace the principal in case of his absence or of temporal or definitive impediment. The same rule will apply when the second alternate representative is to replace the first one, or when the third is to replace the first or second alternates in their turn, or both of them, second. In such cases, the principal representative, or the first or second alternates in their turn, or both of them, shall state their intention not to act as representatives through a declaration given before a Notary Public in Colombia, or before a Notary or another Public Official or a Colombian Consul abroad; and in case of impediment, with the respective certificate. If any of the appointees

COLOMBIA
NOTARIA SEXTA DEL CIRCULO DE BOGOTA
BOGOTA, D.C. - REPUBLICA DE COLOMBIA
2 8 AGO. 2009
AMPARO QUINTERO ARTURO
NOTARIA

representación, en su orden, uno u otros según el caso, asumiéndola por el sólo hecho de ejercerla, cesando en ese momento el ejercicio de la representación por el primero, segundo o tercer suplente en su caso.

Además, confiero (conferimos) poder a los abogados arriba nombrados, para obtener la protección de mi (nuestra) propiedad industrial y contra la competencia desleal, a cuyo efecto autorizo (amos) a los dichos apoderados para que me (nos) representen ante cualesquiera entidades o personas, ejerzan o no jurisdicción, especialmente ante las del orden administrativo, contencioso administrativo y judicial, así como los tribunales de arbitramento, en todo lo concerniente a los siguientes asuntos: a) Obtención de patentes de invención, modelos de utilidad y diseños industriales; el registro de marcas de fábrica, colectivas, defensivas, de servicio, lemas comerciales, nombres comerciales, enseñas, nombres de dominio, variedades vegetales y denominaciones de origen; su renovación, traspaso, cambio de nombre o domicilio, cancelación voluntaria; y el registro de licencias de uso de esos derechos; b) Las acciones de competencia desleal, protección del consumidor, oposiciones u observaciones, cancelación administrativa o judicial, nulidad, medidas cautelares, concesión de licencias, la tutela, la protección de secretos industriales, y en general los juicios civiles, penales, administrativos o contencioso administrativos relacionados con estos derechos; acciones y procesos que promovamos o se nos muevan. Y para que en todos los asuntos arriba determinados, puedan sustituir este mandato, transigir, conciliar, admitir los hechos del proceso, desistir, cancelar, recibir, renunciar, y ratificar los actos de agentes oficiosos.

Dado y firmado hoy _____

en _____

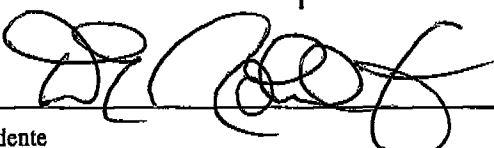
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following alternate shall take his place. When the absence or impediment of the principal representative, or of the first or second alternate in their turn ceases, the representation can be taken again in their sequence, by the principal, the first or second alternate depending on case, and the mere fact or its exercise will suffice. The exercise of the representation by the first, second or third alternates in their turn shall end at such time.

In addition, we grant a Power of Attorney in favor of the above named attorneys at law so that they may obtain the protection of my (our) industrial property and against the unfair competition, for which purpose I (we) authorize the said attorneys to represent me (us) before any authorities or persons, with or without jurisdiction, specially those administrative, administrative contentious and judicial, as well as before Arbitration Court, in all matters concerning the following: a) Obtainment of patents, utility models and industrial designs; the registration of trademarks, collective, defensive and service marks, slogans, commercial names, trade emblems, domain names, vegetal varieties and denominations of origin; its renewal, assignment, change of name or domicile, voluntary cancellation; and the registration of licenses of use of the above rights; b) Actions of unfair competition, protection to the consumer, oppositions or observations, administrative or Court cancellation, nullity, infringement, granting of licenses, the action for writ mandamus, the protection of trade secrets, and in general the civil, penal, and administrative suits relating to those rights; actions and suits instituted by me (us) or against me (us). And that in all the above matters they may substitute this Power of Attorney, compromise, conciliate, admit the facts of the case, desist, cancel, receive, resign, and ratify acts done by representatives without a power of attorney.

Given and signed this March 27, 2009

in Houston, Texas, United States of America


Cedente Assignor

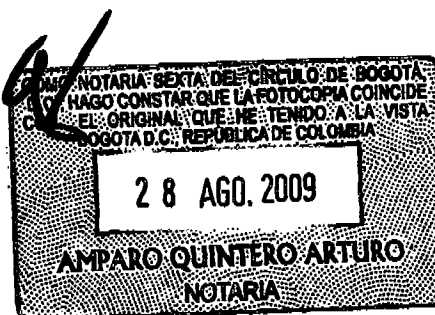
David E. Roberts, Jr. - Executive Vice President

MARATHON OIL COMPANY


Cesionario Assignee

Raymond T. Brickey - President

MARATHON GTF TECHNOLOGY, LTD.



2012

CERTIFICACIÓN NOTARIAL (SOCIEDAD)

El infrascrito Notario Certifica: Que la firma que antecede de _____
es auténtica; que el signatario desempeña actualmente el cargo
de _____
de la compañía _____
sociedad que actualmente existe y está organizada de acuerdo a
las leyes de _____
que la dirección de dicha compañía es _____
y que el signatario tiene facultad para otorgar este documento.

Todos los hechos anteriores le constan por haber examinado los
documentos respectivos y de todo ello da fe.

Dado y firmado en _____

El _____

NOTARIAL CERTIFICATION (COMPANY)

The undersigned Notary certifies: That the preceding signature
of David E. Roberts, Jr.
is authentic, that the signatory currently acts in the position of _____
Executive Vice President
of the company
MARATHON OIL COMPANY
a company currently existing and organized under the laws of
the State of Ohio, United States of America

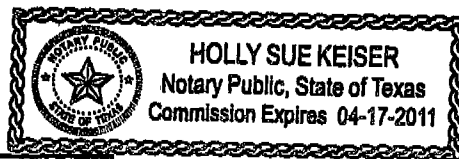
that the address is
5555 San Felipe, Houston, Texas 77056-2799, United States of America
and that the signatory has the power to grant this document.

The Notary Public is aware and attests to the above facts upon
examination of the corresponding documents.

Given and signed in Houston, Texas
United States of America

On March 26, 2009

Holly Keiser
El Notario Público - The Notary Public
(Firma-sello) (Signature-seal)
Name of Notary: HOLLY KEISER

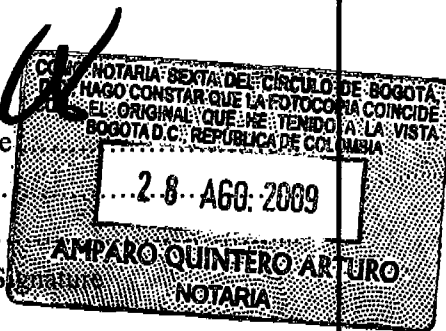


APOSTILLE
(Convention de La Haye du 5 octobre 1961)

- Country: _____
This public document
- has been signed by _____
- acting in the capacity of _____
- bears the seal/stamp of _____

Certified

- at _____
- by _____
- No. _____
- Seal/stamp _____
6. the _____
10. Signature _____



202
203

CERTIFICACIÓN NOTARIAL (SOCIEDAD)

El infrascrito Notario Certifica: Que la firma que antecede de _____
es auténtica; que el signatario desempeña actualmente el cargo
de _____
de la compañía _____,
sociedad que actualmente existe y está organizada de acuerdo a
las leyes de _____,
que la dirección de dicha compañía es _____,
y que el signatario tiene facultad para otorgar este documento.

Todos los hechos anteriores le constan por haber examinado los
documentos respectivos y de todo ello da fe.

Dado y firmado en _____

NOTARIAL CERTIFICATION (COMPANY)

The undersigned Notary certifies: That the preceding signature
of Raymond T. Brickey
is authentic, that the signatory currently acts in the position of _____
President
of the company
MARATHON GTF TECHNOLOGY, LTD.
a company currently existing and organized under the laws of
the State of Delaware, United States of America

that the address is
5555 San Felipe, Houston, Texas 77056-2799, United States of America

and that the signatory has the power to grant this document.

The Notary Public is aware and attests to the above facts upon
examination of the corresponding documents.

Given and signed in Houston, Texas
United States of America

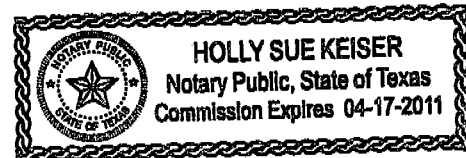
On March 27, 2009

El Notario Público
(Firma-sello)

The Notary Public
(Signature-seal)

Name of Notary: HOLLY KEISER

Holly Keiser



APOSTILLE

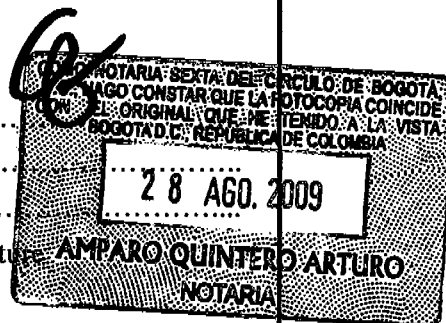
(Convention de La Haye du 5 octobre 1961)

- Country: _____
This public document
- has been signed by _____
- acting in the capacity of _____
- bears the seal/stamp of _____

Certified

- at _____
- by _____
- No. _____
- Seal/stamp _____

- the _____
- Signature _____



203
224

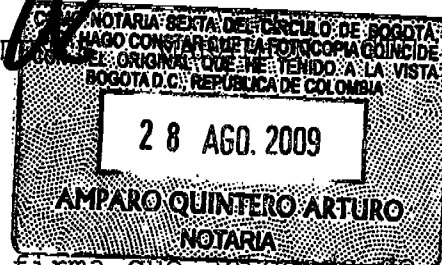
TRADUCCIÓN OFICIAL 227/2009 DE UN DOCUMENTO ESCRITO EN INGLES REALIZADA POR EDUARDO CALADO NOGUERA, TRADUCTOR OFICIAL APROBADO POR RESOLUCIÓN 541 DEL 27 DE FEBRERO DE 1976 EXPEDIDA POR EL MINISTERIO DE JUSTICIA Y DEBIDAMENTE INSCRITO ANTE EL MINISTERIO DE RELACIONES EXTERIORES, MEDIANTE EL CUAL **MARATHON OIL COMPANY**, DOMICILIADA EN 5555 SAN FELIPE, HOUSTON, TEXAS 77056-2799, ESTADOS UNIDOS DE AMERICA, AQUÍ LLAMADO EL CEDENTE, PROPIETARIO DE LAS SOLICITUDES DE PATENTE 06101820 Y 08039674 EN COLOMBIA, LLAMADAS TAL COMO SIGUE:

PROCESO PARA CONVERTIR ALCANOS GASEOSOS A HIDROCARBUROS LÍQUIDOS Y PROCESO PARA CONVERTIR ALCANOS GASEOSOS A OLEFINAS E HIDROCARBUROS LÍQUIDOS, DECLARA POR EL PRESENTE QUE CEDE DICHAS SOLICITUDES A **MARATHON GTF TECHNOLOGY, LTD**, UNA SOCIEDAD CONSTITUIDA Y EXISTENTE DE CONFORMIDAD CON LAS LEYES DEL ESTADO DE DELAWARE, ESTADOS UNIDOS DE AMÉRICA Y DOMICILIADA EN 5555 SAN FELIPE, HOUSTON, TEXAS 77056-3799, ESTADOS UNIDOS DE AMERICA, QUE EN ESTE DOCUMENTO LLAMAREMOS EL CESIONARIO, EL CUAL ACEPTA DICHA CESIÓN Y DESIGNA COMO REPRESENTANTES Y APODERADOS A LUZ CLEMENCIA DE PAEZ, TPA. 23555. DANIEL PEÑA, TPA 65620 Y GERMÁN MARÍN, TPA 64239. EXPEDIDO Y FIRMADO HOY 27 DE MARZO DE 2009 EN HOUSTON, TEXAS, ESTADOS UNIDOS DE AMÉRICA. FIRMADO: DAVID E ROBERTS JR, VICEPRESIDENTE EJECUTIVO, MARATHON OIL COMPANY, CEDENTE.

FIRMADO: RAYMOND T. BRICKEY, PRESIDENTE, MARATHON GTF TECHNOLOGY, LTD., CESIONARIO.

CERTIFICACIÓN NOTARIAL (SOCIEDAD)

El infrascrito notario certifica que la firma que antecede de DAVID E. ROBERTS, JR, es auténtica, que el signatario



Eduardo Calado N.
Eduardo Calado Noguera
TRADUCTOR OFICIAL
Inglés - Español - Inglés
Res. 541 Febrero de 1976

204
205

desempeña actualmente el cargo de vicepresidente ejecutivo de la compañía MARATHON OIL COMPANY, una sociedad actualmente existente y organizada de conformidad con las leyes del estado de OHIO, Estados Unidos de América, que el domicilio de dicha compañía es 5555 SAN FELIPE, HOUSTON, TEXAS 77056-2799, ESTADOS UNIDOS DE AMÉRICA y que el signatario tiene facultad para otorgar este documento.

Todos los hechos anteriores le constan por haber examinado los documentos respectivos y de todo ello da fe.

Dado y firmado en Houston, Texas, Estados Unidos de América, el 26 de marzo de 2009.

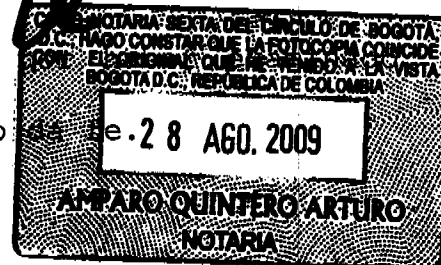
El notario público: HOLLY KEISER

SELLO: HOLLY SUE KEISER, notario público, estado de Texas, El cargo vence 17 de abril de 2011.

CERTIFICACIÓN NOTARIAL (SOCIEDAD)

El infrascrito notario certifica que la firma que antecede de RAYMOND T. BRICKEY, es auténtica, que el signatario desempeña actualmente el cargo de presidente de la compañía MARATHON GTF TECHNOLOGY LTD, una sociedad actualmente existente y organizada de conformidad con las leyes del estado de DELAWARE, Estados Unidos de América, que el domicilio de dicha compañía es 5555 SAN FELIPE, HOUSTON, TEXAS 77056-2799, ESTADOS UNIDOS DE AMÉRICA y que el signatario tiene facultad para otorgar este documento.

Todos los hechos anteriores le constan los documentos respectivos y de todo ello



Eduardo Calado

Eduardo Calado Noguera
TRADUCTOR OFICIAL
Inglés - Español - Inglés
Res. 541 Febrero de 1976

Dado y firmado en Houston, Texas, Estados Unidos de América,
el 27 de marzo de 2009.

El notario público: HOLLY KEISER

SELLO: HOLLY SUE KEISER, notario público, estado de Texas, El
cargo vence 17 de abril de 2011.

EL ESTADO DE TEXAS

SECRETARIA DE ESTADO

No es para usar en los Estados Unidos de América.

Esta apostilla sólo certifica la firma, la calidad del
firmante y el sello o estampilla que lleva. No certifica el
contenido del documento para el cual fue expedido.

APOSTILLA

(Convención de La Haya del 5 de octubre de 1961)

1. País: ESTADOS UNIDOS DE AMÉRICA

Este documento público

2. ha sido firmado por HOLLY KEISER

3. quien actúa en calidad de notario público, estado de Texas

4. y lleva el sello/estampilla de HOLLY KEISER, notario
público, estado de Texas. Mi nombramiento dura hasta el 17 de
abril de 2011.

CERTIFICADO

5. En Austin, Texas.

6. el 24 de abril de 2009

7. por el secretario del estado de Texas.

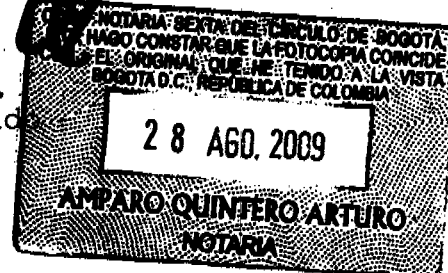
8. Certificado No. N-694669

9. Sello: EL ESTADO DE TEXAS.

10. Firma: HOPE ANDRADE, secretario de estado

ECN\ECN\ID-156800\WPCL002G

Bogotá, 26 de agosto de 2009.



Edmundo Calado

Edmundo Calado Noguera
TRADUCTOR OFICIAL
Inglés - Español - Inglés
Res. 541 Febrero de 1976

SUPERINTENDENCIA DE INDUSTRIA Y COMERCIO

NIT : 800176089-2

RECIBO OFICIAL DE CAJA : 09 - 57,048
FECHA : AGOSTO 3 DE 2009

SUPERINTENDENCIA DE INDUSTRIA Y COMERCIO



No. 06-101820-00005-0000

Fecha 2009-08-31 16:42:05 Dep 2020 NUECLACIONI
Ira 11 PATENTEIYII Eve: 379 FASENACIONALII
Act. 329 C/O INFORMACION Foliós: 10

***** CONSIGNACION *****

DEPOSITANTE	TIPO PAGO	BANCO	CUENTA	No. PAGO	FECHA PGO	Vr. PAGO
CAVELIER ABOGADOS	CONSIGNACION	BANCO DE BOGOTA	062754387	10524500	03/08/2009	20,080,000.00

***** C O N C E P T O *****

CANT. RENTISTICO	CONCEPTO	TOTAL CONCEPTO
1 50005-01-03 CAMBIO DE MODALIDAD Y MODIFICA	12 MARCAS Y LEMAS COMERCIALES	111,000.00
	TOTAL :	\$ 111,000.00

SON: CIENTO ONCE MIL PESOS

RESPONSABLE : _____

RECIBO DE CAJA APLICADO AL EXPEDIENTE No. _____

COLO: 17184-843-001-S

DIVISIÓN DE NUEVAS CREACIONES

RADICACIÓN EXPEDIENTE No. 06-101820

EL EXTRACTO DE LA PRESENTE SOLICITUD DE **PATENTE DE INVENCION**

FUE PUBLICADO EN LA GACETA DE PROPIEDAD INDUSTRIAL No **587** DE

FECHA **18 DE ENERO DE 2008** EL TÉRMINO HÁBIL SEÑALADO POR LA LEY

EXPIRA EL **16 DE ABRIL DE 2008**

NOTA: Dentro del plazo de los seis (6) meses siguientes a partir de la fecha de publicación en la gaceta de Propiedad Industrial, deberá solicitar y cancelar el examen de patentabilidad so pena de que la solicitud caiga en abandono, de acuerdo con lo establecido en el Artículo 44 de la Decisión 486/2000.

SE PRESENTARON OPOSICIONES POR PARTE DE TERCEROS.

SI _____

NO X

**SUPERINTENDENCIA DE INDUSTRIA Y COMERCIO
DIVISIÓN DE NUEVAS CREACIONES**

2020

Bogotá, D. C., 21 de octubre de 2009

Doctor

Emilio Ferrero

Representante **MARATHON OIL COMPANY**

ASUNTO

Radicación 06-101820

Trámite 002

Evento 001

Actuación 430

Oficio 12203

Folios 036

Patente de Invención

☒

Patente de Modelo de Utilidad

☐

Vía Nacional

☐

Vía PCT (fase nacional)

☒

Cap. I

☐

Cap. II

☒

No. Sol. Internacional

PCT/US2005/012655

Fecha de Presentación Internal.

15 de abril de 2005

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: 72 a 117 tal como se radicó inicialmente

1.2. Reivindicaciones: Folios 128 a 137 tal como se radicó inicialmente

1.3. Dibujos: Folios 139 a 153 tal como se radicó inicialmente

1.4. Prioridad:

1.4.1. Fecha 16 de abril de 2004
País Estados Unidos
Número 10/826885

1.4.2. Fecha 8 de abril de 2005
País Estados Unidos
Número 11/101886

2. Análisis de la Prioridad

- La prioridad 10/826885 será tenida en cuenta para las reivindicaciones 1 a 20
- La prioridad 11/101886 será tenida en cuenta para las reivindicaciones 21 a 42

3. Objeto de la invención

- Título de la solicitud (*folio 1*)
Proceso para convertir alcanos gaseosos en hidrocarburos líquidos
- Las reivindicaciones 1 a 42 de la solicitud en estudio se refieren a
 - 1.- Un proceso para convertir alcanos gaseosos a hidrocarburos líquidos que comprende:
 - Reacción de una alimentación gaseosa que tiene alcanos de mas bajo peso molecular con vapor de bromo para formar bromuros de alquil y ácido bromhídrico; y
 - Reacción de dichos bromuros de alquil y ácido bromhídrico en la presencia de un catalizador de aluminosilicato cristalino sintético y *a una temperatura suficiente* para formar hidrocarburos de más alto peso molecular y vapor de ácido bromhídrico
 - 18.- Un proceso para convertir alcanos de más bajo peso molecular a hidrocarburos líquidos que comprende:
 - Reacción de una alimentación gaseosa que tiene alcanos de bajo peso molecular con vapor de bromo para formar bromuros de alquil y ácido bromhídrico; y
 - Reacción de dichos bromuros de alquil y ácido bromhídrico en la presencia de un catalizador de aluminosilicato cristalino sintético *** para formar hidrocarburos de más alto peso molecular y vapor de ácido bromhídrico
 - *Conversión de dicho ácido bromhídrico a bromo*
 - 21.- Un proceso para convertir alcanos gaseosos a hidrocarburos líquidos que comprende:
 - Reacción de una alimentación gaseosa que tiene alcanos de bajo peso molecular con vapor de bromo para formar bromuros de alquil y ácido bromhídrico; y
 - Reacción de dichos bromuros de alquil y ácido bromhídrico en la presencia de un catalizador de aluminosilicato cristalino sintético y a una temperatura suficiente para formar hidrocarburos de más alto peso molecular y vapor de ácido bromhídrico
 - *Remoción del vapor de ácido bromhídrico mencionado de los hidrocarburos de más alto peso molecular mencionados por reacción del mencionado vapor de ácido bromhídrico con un óxido de metal para formar un bromuro de metal y vapor*
 - 27.- Un proceso para convertir los alcanos gaseosos a hidrocarburos líquidos que incluye:
 - Reacción de una alimentación gaseosa que contiene alcanos de bajo peso molecular con vapor de bromo para formar bromuros de alquil y ácido bromhídrico; y
 - Reacción de dichos bromuros de alquil y ácido bromhídrico en la presencia de un catalizador de aluminosilicato cristalino sintético y a una temperatura suficiente para formar hidrocarburos de más alto peso molecular y vapor de ácido bromhídrico y
 - *Transporte de dicho vapor de ácido bromhídrico y los hidrocarburos de más alto peso molecular mencionados a un primer recipiente que tiene un lecho de partículas de óxido de metal, dicho vapor de ácido bromhídrico reacciona con el lecho de partículas de óxido de metal, dicho vapor de ácido bromhídrico reacciona con el lecho de partículas de óxido de metal mencionado para formar partículas de bromuro de metal y vapor.*

- 35.- Un proceso para convertir alcanos gaseosos a hidrocarburos líquidos que incluye:

- Reacción de una alimentación gaseosa que tiene alcanos de bajo peso molecular con vapor de bromo para formar bromuros de alquil y ácido bromhídrico; y
- Reacción de dichos bromuros de alquil y ácido bromhídrico en la presencia de un catalizador de aluminosilicato cristalino sintético y a una temperatura suficiente para formar hidrocarburos de más alto peso molecular y vapor de ácido bromhídrico y
- *Remover dicho vapor de ácido bromhídrico de los hidrocarburos de más alto peso molecular mencionados mediante reacción con un óxido de metal para un primer bromuro de metal y vapor*
- *Oxidar dicho primer bromuro de metal con un gas que contiene oxígeno para formar vapor de bromo y*
- *Reaccionar dicho vapor de bromo con un bromuro de metal reducido para formar un segundo bromuro de metal*

- Los anteriores procedimientos buscan *obtener combustibles líquidos a partir de alcanos como el metano.*
- La Clasificación Internacional de Patentes (IPC) para esta solicitud es C07C1/00.

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:

- Por su estructura todas las reivindicaciones deben constar de dos partes. Una primera parte, el preámbulo, sirve para situar el objeto de la invención dentro de un contexto técnico, es lo que se conoce y sobre lo que no se reclama ningún privilegio. La segunda parte, o parte característica, define lo que se considera novedoso y se desea proteger. Estas dos partes están separadas por expresiones como 'caracterizado por' o similares. En las reivindicaciones, especialmente las independientes no se observa la diferencia entre lo que el solicitante considera nuevo de lo que considera conocido. Se recomienda corregir todo el capítulo.
- No se precisa la materia sobre la cual se solicita protección. Cómo se explicará en el punto 4), la presente solicitud no posee unidad de invención, por lo que no está definida la materia sobre la cual se solicita protección.
- La reivindicación independiente se refiere a la invención que el solicitante desea proteger, mientras que las reivindicaciones dependientes son formas particulares de la invención de la reivindicación de la cual dependen. En la presente solicitud, el solicitante refiere reivindicaciones independientes con objetos de solicitud, pero las reivindicaciones dependientes de ellas no relacionan formas particulares de esa invención sino procesos adicionales que corresponderían a objetos diferentes de la reivindicación de la cual dependen. Esto es inadmisibile. Lo anterior sucede con las reivindicaciones 11, 13, 16, 17, 19, 25, 28, 29, 30, 31, 32, 33, 36, 37, 38, 39, 41 y 42. Esto conlleva a que las reivindicaciones mencionadas son falsas dependencias porque corresponden a procesos diferentes al proceso objeto de la reivindicación principal.
- El solicitante es sumamente ambiguo en la presentación de su solicitud, por ejemplo

- Habla de alcanos de más bajo peso molecular. Distintos técnicos pueden interpretar de forma diferente esta frase; para algunos podrían ser alcanos por debajo de cinco carbonos, para otros por debajo de 10 o para otros por debajo de veinte, etc. El solicitante debe ser explícito en referir el tipo de alcanos objeto de su solicitud.
- Habla de temperatura suficiente. Deberá el solicitante ser explícito en determinar el rango de temperaturas, pues también puede interpretarse de varias formas su afirmación.
- No es válido el uso de frases como "cerca de" o similares; deberán eliminarse.

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. Unidad de invención (Artículo 25 D. 486)

La presente solicitud no tiene unidad de invención, dado que contempla diferentes conceptos inventivos relacionados así:

- *Reivindicación 1 y dependientes.*
- *Reivindicación 18 y dependientes.*
- *Reivindicación 21 y dependientes.*
- *Reivindicación 27 y dependientes.*
- *Reivindicación 35 y dependientes.*

Entre ellos no existe una relación dado que:

- La reivindicación 18 relaciona la conversión de dicho ácido bromhídrico a bromo y no contempla la temperatura, a diferencia de lo relacionado en la reivindicación 1.
- La reivindicación 21 relaciona la remoción del vapor de ácido bromhídrico de los hidrocarburos de más alto peso molecular por reacción del vapor de ácido bromhídrico con un óxido de metal para formar un bromuro de metal y vapor, algo que no relacionan ni la reivindicación 1 ni la 18.
- La reivindicación 27 relaciona el transporte del vapor de ácido bromhídrico y los hidrocarburos de más alto peso molecular a un primer recipiente que tiene un lecho de partículas de óxido de metal, dicho vapor de ácido bromhídrico reacciona con el lecho de partículas de óxido de metal, dicho vapor de ácido bromhídrico reacciona con el lecho de partículas de óxido de metal para formar partículas de bromuro de metal y vapor. Esto no lo enseña ni las reivindicaciones 1, 18, ni 21.
- La reivindicación 35 señala como parte del proceso -Remover vapor de ácido bromhídrico de los hidrocarburos de más alto peso molecular mediante reacción con un óxido de metal para un primer bromuro de metal y vapor - Oxidar el primer bromuro de metal con un gas que contiene oxígeno para formar vapor de bromo y - Reaccionar dicho vapor de bromo con un bromuro de metal reducido para formar un segundo bromuro de metal. Estas etapas no las contemplan ni las reivindicaciones 1, 18, 21 o 27

Por lo anterior, se puede concluir que la presente solicitud no cumple con el requisito de unidad de invención. El solicitante debería presentar una única reivindicación independiente dirigida a un único proceso y a partir de allí determinar formas particulares de dicho proceso, o, dividir su solicitud si lo considera.

6. Determinación del Estado de la Técnica

- La fecha que se ha tenido en cuenta para determinar el estado de la técnica es
 - 16 de abril de 2004 para las reivindicaciones 1 a 20
 - 8 de abril de 2005 para las reivindicaciones 21 a 42
- Teniendo en cuenta la fecha indicada se realizó **UNA BÚSQUEDA PRELIMINAR** 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	George Olah Árpád Molnár	Hydrocarbon Chemistry	2003
D2	Henry Rakoff Norman Rose	Química Orgánica fundamental	1966
D3	US 4 465 893	Oxidative condensation of natural gas or methane into gasoline range hydrocarbon	14.08.1984
D4	US 3 894 107	Conversion of alcohols, mercaptans, sulfides, halides and/or amines	08.07.1975
D5	GB 1104294	Production of lower alkanols and lower alkyl bromides	21.02.1964

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

Si bien no es posible realizar un correcto estudio de patentabilidad por todo lo reseñado en los puntos 4 y 5, una primera aproximación a la solicitud permite inferir de forma preliminar que no se cumplirían los requisitos para que se le conceda el privilegio solicitado.

Aunque, como ya se afirmó en el punto 5, el solicitante relaciona varios procesos diferentes, existen algunos pasos comunes sobre los que se basaría la solicitud. Estos pasos son la reacción de alcanos de uno a cinco carbonos (de acuerdo a lo referido en el folio 80) con bromo para formar alquil bromuros y ácido bromhídrico y luego hacer reaccionar estos dos productos con un catalizador de aluminosilicato cristalino sintético o zeolita (especialmente ZSM-5) para formar hidrocarburos de más alto peso molecular y ácido bromhídrico o bromo que puede usarse nuevamente en el proceso.

En referencia a estas dos reacciones secuenciales se tiene lo siguiente:

- La primera reacción relacionada es de uso común en el arte y cualquier técnico medio la conoce. Esto lo demuestra:
 - Que el mismo solicitante la refiere como conocida; cita la patente US5998679 (folio 75) para bromar alcanos, las patentes US6462243, US6472572, US6525230 para alcanzar compuestos monohalogenados útiles en posteriores reacciones, o también las patentes US4655893 y US4467130. Nótese que también aquí habría falta de sustento en la descripción, porque lo que en las reivindicaciones se considera nuevo en la misma descripción el solicitante dice que no lo es.
 - Que en la técnica se conoce esta reacción ampliamente. Se cita el documento D5 como ejemplo.
 - Que un técnico medio aprende en su química básica que un alcano reacciona con cloro o bromo dando origen a alcanos halogenados y desprendiendo halogenuros de hidrógeno. Por consiguiente, el documento referido aquí como D2 señala el conocimiento medio de un experto en el arte.
- La segunda reacción también es conocida. Esto lo demuestra:

- Que el mismo solicitante la refiere como conocida; cita en el folio 76 que alcanos sustituidos se pueden convertir en hidrocarburos con rango de ebullición de olefinas y gasolinas sobre diversas formas de silicato de aluminio cristalino (zeolitas) empleándose habitualmente ZSM-5.
- Que existen anterioridades tales como D4 que relacionan que compuestos como haluros alifáticos se pueden convertir en productos orgánicos de peso molecular mucho mayor con ayuda de zeolitas.
- El documento D1 (del 2003) relaciona las dos reacciones para convertir inicialmente compuestos como el metano, o alcanos de 1 a 5 carbonos, en haluros de alquilo (ejemplifica con cloruro o bromuro de metilo) y luego empleando uno de muchos catalizadores (que incluye zeolitas y aun más específicamente ZSM-5) en hidrocarburos de pesos moleculares mayores, que podría ser del tamaño de los que configuran la gasolina.
- El documento D3 describe las dos reacciones de forma simultánea (columna 4), configurando el mismo proceso que sería objeto de la solicitud.

De lo anterior se tiene que la solicitud no cumpliría con los requisitos de patentabilidad para que se le concediera el privilegio solicitado.

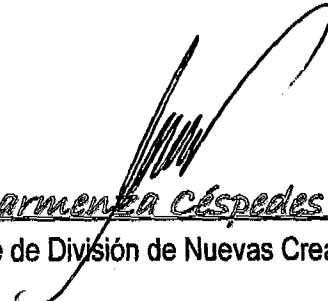
8. Conclusión:

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

N°	Documento N°	Reivindicaciones afectadas	Requisito que afecta
D1	George Olah Árpád Molnár	1 - 42	Novedad
			Nivel inventivo
D2	Henry Rakoff Norman Rose	1 - 42	Novedad
			Nivel inventivo
D3	US 4 465 893	1 - 42	Novedad
			Nivel inventivo
D4	US 3 894 107	1 - 42	Novedad
			Nivel inventivo
D5	GB 1104294	1 - 42	Novedad
			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.


Alix Carmona Céspedes De Vergel
 Jefe de División de Nuevas Creaciones

Concepto Técnico No. **3668**

Examinador Técnico **202003**

El anterior requerimiento fue notificado por fijación en lista, de fecha

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HYDROCARBON CHEMISTRY

SECOND EDITION

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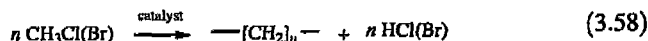
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3.5.2. Hydrocarbons through Methyl Halides

It has been demonstrated that methyl chloride or bromide can be dehydrohalogenatively condensed into hydrocarbons over acidic catalysts:



One important prerequisite to the application of this reaction in hydrocarbon synthesis is the selective monochlorination of methane. Usual radical chlorination of methane is not selective, and high $\text{CH}_4 : \text{Cl}_2$ ratios are needed to minimize formation of higher chlorinated methanes (see Section 10.2.5). In contrast with radical halogenation, electrophilic halogenation of methane was shown to be a highly selective process.⁴¹²

A range of superacid catalysts such as $\text{NbOF}_3\text{--Al}_2\text{O}_3$, $\text{ZrOF}_2\text{--Al}_2\text{O}_3$, $\text{SbF}_5\text{--graphite}$, and $\text{TaF}_5\text{--Nafion-H}$ effect the chlorination and bromination of methane.^{411,413} $\text{ZrOF}_2\text{--Al}_2\text{O}_3$ gives the best results in chlorination (96% selectivity at 34% conversion), and $\text{SbOF}_3\text{--Al}_2\text{O}_3$ is the best for bromination (99% selectivity at 20% conversion). Supported platinum and palladium catalysts are also very effective with selectivities also exceeding 90% (99% selectivity at 36% conversion over 0.5% platinum on alumina at 250°C, with a feed composition of $\text{CH}_4 : \text{Cl}_2 = 3 : 1$).⁴¹¹ Solid acids and zeolites have also been found to be very selective in monochlorination.^{476,477}

Hydrogen chloride formed during the chlorination of methane must be oxidized to chlorine, either in the oxychlorination of methane⁴⁷⁸ or in a separate Deacon-type operation to allow the process to become economical. This is still difficult to achieve. Existing data also show that formation of higher chlorinated methane derivatives is often also a difficulty of the reaction.⁴⁷⁹⁻⁴⁸¹ These difficulties can be minimized by using bromine in the catalytic oxidative conversion process.

Hydrocarbon formation from methyl chloride can be catalyzed by ZSM-5 ^{482,483} or bifunctional acid-base catalysts such as WO_3 on alumina.^{420,447} The reaction on ZSM-5 gives a product distribution (43.1% aliphatics and 57.1% aromatics at 369°C) that is very similar to that in the transformation of methanol, suggesting a similar reaction pathway in both reactions.⁴⁸³ WO_3 on Al_2O_3 gives 42.8% $\text{C}_2\text{--C}_5$ hydrocarbons at 327°C at 36% conversion.⁴⁴⁷ When using methyl bromide as the feed, conversions are comparable. However, in this case, HBr can be very readily air-oxidized to Br_2 allowing a catalytic cycle to be operated. Since bromine is the oxidant, the reaction is economical. The "one step" oxidative condensation of methane to higher hydrocarbons was also achieved in the presence of chlorine or bromine over superacidic catalysts.³⁵⁷

3.5.3. Hydrocarbons through Sulfurated Methanes

The ready availability of carbon disulfide from methane and sulfur in oxide-catalyzed reactions⁴⁸⁴ [Eq. (3.59)] and its further transformation over zeolites⁴⁸⁵ [Eq. (3.60)] or other catalysts offer an alternative way to the production of hydrocarbons from methane:

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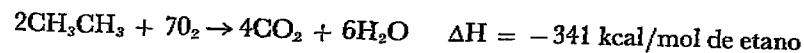
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*A Mary y Myra
por su fe y estímulo, y sobre todo,
por su paciencia.*

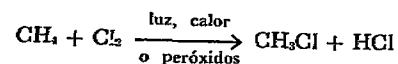
Se dice que los alcanos son **saturados**, ya que tienen en su molécula sólo enlaces sencillos entre dos átomos. Los alcanos no sufren, por consiguiente, reacciones de adición, como la hidrogenación catalítica (Sección 2-11), que es característica de compuestos con enlaces múltiples.

2-14. Oxidación. Los alcanos arden con desprendimiento de grandes cantidades de calor.



El gas natural, la gasolina y el diesel se emplean como combustibles, tanto por esta propiedad de desprender una gran cantidad de calor en la combustión, como porque, en grandes cantidades, es más fácil manejar líquidos que sólidos. Con respecto a su peso, el carbón tiene aproximadamente el 70 por ciento del valor combustible de los alcanos.

2-15. Halogenación. En presencia de **luz**, de **peróxidos orgánicos** o **calentados** a temperaturas de 300° o más, los alcanos reaccionan con cloro o bromo dando origen a alcanos halogenados y desprendiendo halogenuros de hidrógeno.



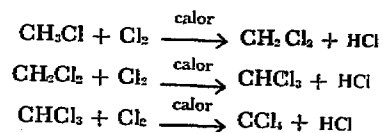
En esta reacción de halogenación, un átomo de halógeno substituye a un hidrógeno. Este tipo de reacción se llama **reacción de substitución**. Como las valencias del carbono están totalmente saturadas en los alcanos, es de esperarse que reaccionen principalmente por substitución. En estas reacciones generalmente se rompen enlaces carbono-hidrógeno pero no enlaces carbono-carbono.

El yodo no reacciona con los alcanos y el flúor reacciona con tanta violencia para dar los compuestos fluorados, que resulta sumamente difícil controlar la reacción y puede haber explosiones. Los productos de la reacción de fluoración difieren de los obtenidos en la bromación y en la cloración en que frecuentemente se originan rupturas de enlaces carbono-carbono, aparte de la ruptura carbono-hidrógeno y, además, se producen cantidades considerables de compuestos **perfluorados**, es decir, compuestos en los que se han substituido todos los átomos de hidrógeno por flúor.



La reacción puede hacerse menos violenta diluyendo al flúor con nitrógeno y usando recipientes adecuados para disipar rápidamente el calor de la reacción.

Además del derivado monohalogenado, se obtienen derivados *di*, *tri* y *poli*-halogenados en reacciones subsecuentes. Por ejemplo, en la cloración del metano se obtienen, además, diclorometano, cloroformo (triclorometano) y tetracloruro de carbono (tetracloro metano), en reacciones subsecuentes.



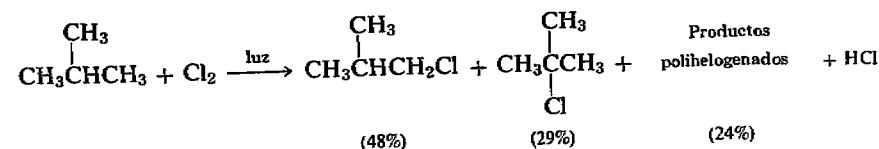
Inicialmente sólo hay moléculas de metano y cloro en el recipiente de reacción, por lo tanto, el único producto posible es el clorometano. Al aumentar la concentración del clorometano aumenta la probabilidad de que el cloro reaccione con una molécula de clorometano, produciéndose diclorometano, puesto que al mismo tiempo, disminuye la probabilidad de que reaccione con el metano, ya que las moléculas de éste comienzan a disminuir en concentración. El cloroformo y el tetracloruro de carbono se producen por reacción del cloro sobre diclorometano y cloroformo, respectivamente. El rendimiento de los productos clorados varía de acuerdo con la proporción de los reactivos, el tiempo que éstos estén en contacto y algunas otras condiciones de reacción. En la Tabla 2-3 se indican las fracciones de mol (número de moles de un producto dividido entre el número total de moles de todos los productos) de los diversos productos clorados obtenidos a partir del metano, a 440°. También se ve en esta Tabla el cambio en la concentración de productos con el cambio de las condiciones de reacción. Los datos de la Tabla 2-3 no indican que todo el metano se haya clorado, sino que muestran la relación en que se obtienen los productos. Por estos datos puede deducirse que es difícil obtener un solo producto, ya que aun disminuyendo la cantidad de cloro se obtiene casi 50 por ciento de productos polihalogenados.

TABLA 2-3
Cloración del Metano a 440°C

RELACIÓN MOLAR	FRACCIONES DE MOL RELATIVAS DE LOS PRODUCTOS				
Cl_2/CH_4	CH_3Cl	CH_2Cl_2	CHCl_3	CCl_4	
.5	.62	.30	.07	.01	
1.10	.37	.41	.19	.03	

Los productos orgánicos que se obtienen en una reacción junto con el producto deseado se conocen como productos secundarios. En este caso, si el producto deseado es el cloruro de metilo, los compuestos polihalogenados se consideran como subproductos. El clorometano, el diclorometano y el cloroformo se obtienen comercialmente mediante la halogenación en fase vapor del metano. El tetracloruro de carbono se obtiene generalmente, haciendo reaccionar sulfuro de carbono con cloro o con monocloruro de azufre, S_2Cl_2 .

La halogenación de los alcanos con tres o más átomos de carbono da una *mezcla* de alcanos monohalogenados isómeros junto con un pequeño porcentaje de derivados polihalogenados.

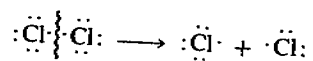


Esta reacción no tiene gran aplicación en el laboratorio, ya que se obtiene siempre una mezcla de productos halogenados. Más adelante se indicarán reacciones más selectivas para la obtención de halogenuros de alquilo, que se pueden usar de preferencia en lugar de la halogenación catalizada por luz.

2-16. Mecanismos de sustitución. En los últimos años, muchos químicos orgánicos se han dedicado a estudiar con gran detalle el mecanismo de un gran número de reacciones químicas. *Un mecanismo de reacción es el camino o pasos sucesivos por los que atraviesan las moléculas al pasar de reactivos a productos.* Se espera que el conocimiento de los pasos por los que atraviesan los reactivos para dar los productos, en una reacción determinada, pueda ayudar a los químicos a predecir las condiciones óptimas de reacción y las reacciones secundarias posibles. El conocimiento de los mecanismos de reacción también permite, tanto al químico como al estudiante, correlacionar un gran número de reacciones que aparentemente no tienen relación alguna. Esta correlación de diferentes reacciones ayuda a disminuir el trabajo de la memoria en forma muy considerable. Un punto muy importante respecto a los mecanismos de reacción, que se debe tener siempre presente es que éstos no son hechos experimentales sino *razonamientos especulativos* basados en los hechos observados. Esto significa que puede haber más de un mecanismo que esté de acuerdo con los hechos observados y que los mecanismos frecuentemente deben modificarse para ponerlos de acuerdo con el descubrimiento de nuevos datos experimentales.

Cualquier mecanismo que se proponga para la halogenación de los alcanos deberá explicar los datos experimentales siguientes: 1) la reacción es muy lenta en la oscuridad y a temperatura ambiente; 2) la reacción es rápida cuando la mezcla se irradia con luz a temperatura ambiente; 3) la reacción también es rápida si la mezcla de reacción se calienta a temperaturas elevadas (más de 300°) en la oscuridad; 4) la reacción puede iniciarse en la oscuridad y a temperaturas inferiores a 150°, mediante la adición de muy pequeñas cantidades de sustancia como tetraetilo de plomo, hexafeniletano o peróxido de benzoilo; 5) se obtienen muchas moléculas de alcano halogenado por cada fotón absorbido, cuando la reacción se inicia con luz.

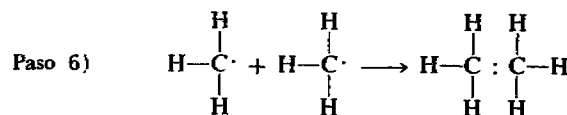
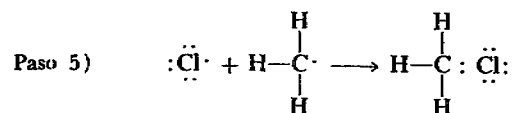
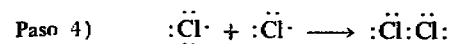
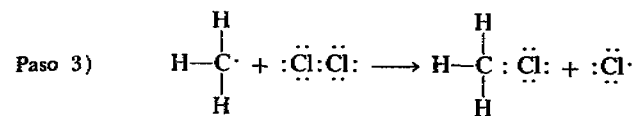
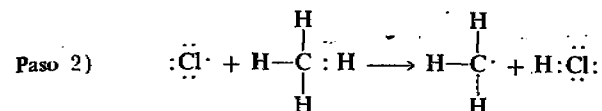
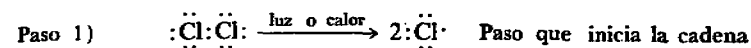
Se cree que se producen radicales libres como intermediarios cuando los alcanos reaccionan con los halógenos. Un **radical libre** es un grupo que tiene, por lo menos, un electrón **no apareado**. El electrón no apareado no implica que exista una carga en el átomo en el que se encuentra. La mayoría de los radicales libres son en extremo reactivos y tienden a asociarse "apareando" el electrón libre. Con pocas excepciones, la vida media de los radicales libres no pasa de milésimas de segundo. Los radicales libres se forman, generalmente, por la *ruptura homolítica* de un enlace covalente, esto es, mediante una ruptura en la cual cada átomo se queda con uno de los electrones del par de enlace.*



La ruptura homolítica de una molécula de cloro produce dos **átomos de cloro**. Estos átomos de cloro son eléctricamente neutros, es decir, no tienen carga positiva ni negativa.

* No todos los radicales libres se forman por ruptura de un enlace covalente. Algunos metales (por ejemplo, sodio y potasio) funcionan como radicales. Una molécula de oxígeno es un radical.

El siguiente mecanismo de reacción para la cloración del metano, explica las observaciones señaladas anteriormente, así como la obtención de los productos, y actualmente es el más aceptado.

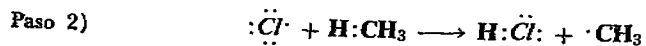
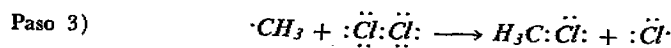
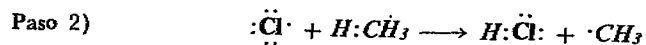
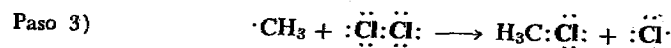
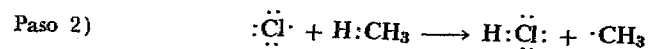


Pasos de
propagación de la cadena

Pasos que terminan la cadena

Esta reacción se **inicia** con la ruptura homolítica de la molécula de cloro para dar dos radicales libres. Para este paso se requiere una energía igual a la *energía de disociación de enlace* de la molécula de cloro. Esta energía puede proporcionarse calentando la mezcla de reacción a una temperatura elevada. A temperatura ambiente se puede proveer esta energía mediante luz, que será absorbida por los electrones de valencia. Generalmente se usa luz ultravioleta y no luz visible ya que la luz ultravioleta tiene más energía por fotón que la luz visible. La formación de los átomos de cloro es una reacción endotérmica ($\Delta H = +58 \text{ kcal/mol}$); por consiguiente, la reacción es muy lenta a temperatura ambiente, en la oscuridad.

Una vez que se forman los radicales libres cloro, éstos pueden reaccionar con las moléculas de metano, como se indica en el Paso 2, produciendo cloruro de hidrógeno (que es uno de los productos de la reacción) y radicales libres metilo. Estos últimos pueden reaccionar, a su vez, con moléculas de cloro, como se indica en el Paso 3, produciendo una molécula de cloruro de metilo (el segundo producto de la reacción total) y otro radical libre cloro. Este nuevo radical libre cloro puede reaccionar con otra molécula de metano, como se indica en el Paso 2, generando una segunda molécula de cloruro de hidrógeno y un segundo radical libre metilo. Una vez que se ha fragmentado una molé-



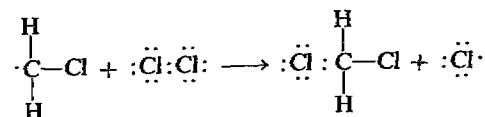
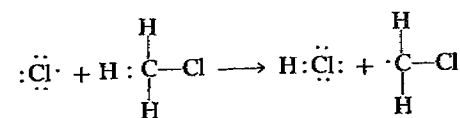
Luego de paso 3, el paso 2, etc.

Esto explica por qué se pueden obtener muchas moléculas de alcano halogenado por cada fotón absorbido por el sistema, cuando la reacción se inicia mediante irradiación con luz.

El Paso 1 se llama de **iniciación de la cadena**, ya que la reacción se inicia con la ruptura de la molécula de halógeno. Los Pasos 2 y 3 se llaman de **propagación de la cadena**, ya que uno de los productos de un paso es el **reactivo** en el siguiente. Los pasos de propagación originan el mismo número de radicales que consumen. Debido a que los intermediarios propuestos para la reacción son radicales libres y a que la repetición de los pasos de propagación origina una larga serie de reacciones, se dice que la halogenación del metano es una **reacción en cadena por radicales libres**. La halogenación de todos los alcanos, ya sea con bromo o cloro, implica un mecanismo análogo al propuesto en el caso de la cloración del metano.

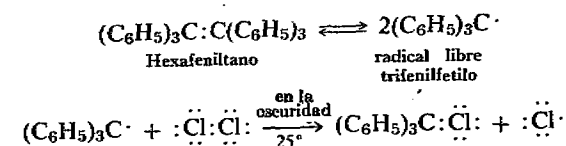
Del mecanismo propuesto puede suponerse que una vez que se inicia la reacción, ésta continúa hasta que se consume todo el halógeno. Sin embargo, esto no ocurre, ya que si se apaga la luz o se enfría la mezcla, la reacción se detiene. La razón de esto es que los radicales libres cloro pueden reaccionar con cualquier sustancia que se encuentre presente. Inicialmente como la concentración de moléculas de alcano es muy grande, los radicales libres cloro reaccionan con éstas antes de chocar con otras moléculas (no se están considerando los choques no productivos entre una molécula de cloro y un radical libre cloro para producir otra molécula de cloro y otro radical libre cloro). En un momento dado hay un número muy pequeño de radicales libres presentes, por lo tanto, la probabilidad de que dos radicales libres cloro choquen entre sí, Paso 4, produciendo una molécula de cloro, es pequeña; sin embargo esta reacción ocurre. Como esta reacción consume radicales libres sin producirlos, se conoce como **terminación de cadena**. El Paso 5, que es la producción de cloruro de metilo por el choque de un radical libre cloro con un radical libre etano, y el Paso 6, la reacción de dos radicales libres metilo para producir etano, son también reacciones de terminación de cadena, ya que consumen radicales libres sin producirlos.

Como la concentración de cloruro de metilo va en aumento, hay una tendencia cada vez mayor a que se produzca un radical libre clorometilo, que puede participar en la propagación de la cadena, dando origen a un alcano polihalogenado.



El hecho de que se produzcan alcanos polihalogenados apoya esta hipótesis.

Si la reacción marcha realmente por el camino descrito, la adición de sustancias que pueden producir radicales libres hará que sean éstas capaces de actuar como iniciadoras de la reacción en la oscuridad y a temperaturas menores de 300°. En 1940, W. Vaughn y F. Rust (de la Shell Development Company) lograron clorar el pentano, a 25° y en la oscuridad, mediante la adición de menos de 0.0001 de mol de hexafeniletano por mol de pentano. El hexafeniletano, en solución se encuentra en equilibrio con radicales libres trifenilmetilo. Los radicales libres trifenilmetilo pueden actuar como iniciadores de la reacción, al descomponer una molécula de cloro para producir cloruro de trifenilmetilo y un radical libre cloro.



El hecho de que el hexafeniletano está en equilibrio con radicales libres trifenilmetilo se puede deducir de sus propiedades químicas y de sus propiedades físicas especiales debidas al electrón no apareado. Este se detecta mediante medidas de susceptibilidad magnética o por resonancia magnética electrónica. La concentración de radicales libres cloro o metilo presentes, cuando se originan estos radicales mediante luz o calor, es muy pequeña y resulta difícil de medir por estos métodos.

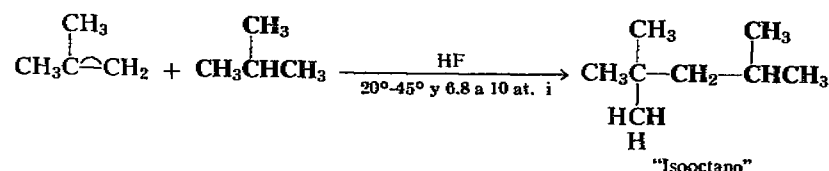
2-17. Velocidad de Reacción. Para completar la exposición acerca de la halogenación de los alcanos, se hace necesario referirse en detalle a la velocidad de reacción y a algunos conceptos relacionados con ésta. La *velocidad de reacción se define como la cantidad de reactivo que se consume en la unidad de tiempo o como la cantidad de producto que se obtiene en la unidad de tiempo*. Si un químico desea obtener 1-cloropropano por cloración del propano, le será de gran utilidad conocer los factores que pueden aumentar el número de moles de 1-cloropropano producidos en una hora. Como se indicó anteriormente, una cosa que se puede hacer es iluminar el matraz de reacción. Otro punto de interés para el químico es la relación entre la velocidad de reacción en la obtención del 1-cloropropano y la velocidad de reacción en la obtención del 2-cloropropano, así como la relación respecto a otras velocidades de reacción en la formación de productos secundarios.

La velocidad de reacción está relacionada con dos factores (aparte de la

ne con un índice de octano mayor que la producida por cracking térmico y en la actualidad se requiere gasolina con un índice de octano mayor, para los nuevos motores de alta compresión.

El cracking de los hidrocarburos para producir compuestos de peso molecular menor, no resulta útil desde el punto de vista de laboratorio, ya que se obtiene una mezcla compleja de productos.

C. ALQUILACIÓN. En presencia de catalizadores ácidos, tales como ácido fluorhídrico (fluoruro de hidrógeno anhidro), los alquenos y alcanos de bajo peso molecular, que se obtienen del cracking, se pueden condensar para dar hidrocarburos ramificados con un elevado índice de octano.



Estas gasolinas de alto índice de octano se mezclan con la gasolina obtenida por destilación directa y las gasolinas de cracking catalítico.

2-28. Índice de octano. Una de las características deseables de un combustible destinado para motores de combustión interna es que entre en combustión sólo después de que se inicie ésta mediante la chispa de la bujía y que, una vez iniciada la combustión, ésta sea uniforme, de tal manera que la fuerza aplicada sobre el pistón resulte uniforme y continua. Algunas gasolinas no tienen este comportamiento sino que arden prematuramente o detonan en vez de arder en forma suave. Estos combustibles se dice que "detonan". La tendencia de un combustible a detonar se indica mediante el índice de octano. Como el *n*-heptano detona fuertemente en un motor de prueba tipo y en condiciones prefijadas, se le asigna un índice de octano de 0. En cambio el 2,2,4-trimetilpentano (mal llamado isooctano en la industria petrolera) arde suavemente, por lo que se le asigna un índice de octano de 100. El índice de octano de un combustible determinado que se somete a prueba se define como el porcentaje de isooctano (en volumen) que debe agregarse al *n*-heptano para dar las mismas características detonantes que el combustible de prueba. Como se ve en la Tabla 2-6, el índice de octano *aumenta al disminuir el peso molecular y aumentar las ramificaciones*

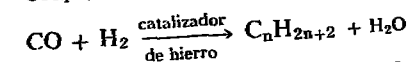
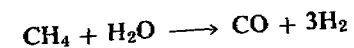
Los alquenos, cicloalcanos e hidrocarburos aromáticos tienen índices de octano elevados.

TABLA 2-6
Índice de Octano de los Hidrocarburos

HIDROCARBUROS	INDICE DE OCTANO	HIDROCARBUROS	INDICE DE OCTANO
Metano	100+	Octano	-17
Propano	99.5	3-Metilheptano	35

El índice de octano de los combustibles se puede aumentar mediante la adición de una pequeña cantidad de *tetraetilo de plomo*, $(\text{CH}_3\text{CH}_2)_4\text{Pb}$. La gasolina que contiene este aditivo se conoce como gasolina "etílica". El comportamiento exacto del tetraetilo de plomo no se conoce.

2-29. Proceso Fischer-Tropsch. Si las reservas de petróleo mundiales se agotaran, sería necesario obtener en forma sintética grasas, aceites lubricantes y combustibles líquidos. En 1923, F. Fischer y H. Tropsch, trabajando para el Instituto de Investigación del Carbón de Piedra "Kaiser-Wilhelm", encontraron que es posible obtener hidrocarburos para gasolina, combustible diesel, y muchos compuestos oxigenados, mediante la hidrogenación del monóxido de carbono en presencia de hierro, níquel o cobalto, como catalizadores. El monóxido de carbono que se requiere para este proceso se obtiene haciendo reaccionar el gas natural o el carbón de piedra con vapor de agua.



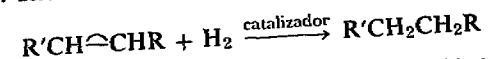
El monóxido de carbono debe reducirse y los átomos de carbono unirse entre sí para formar las cadenas de carbono de los productos. El obstáculo principal para el uso comercial del proceso Fischer-Tropsch es el elevado costo inicial de la planta (de dos a cinco veces más que una refinería convencional).

Resumen de reacciones

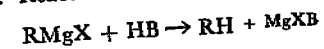
Alcanos.

Preparación.

A. Reducción catalítica de alquenos

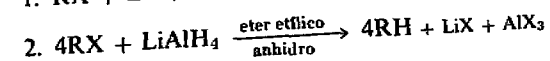
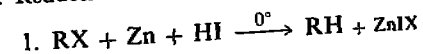


B. Reactivos de Grignard e hidrógenos "ácidos".



HB puede ser HOH, ROH, RCOOH, RNH₂, o también otras fuentes de hidrógenos ácidos.

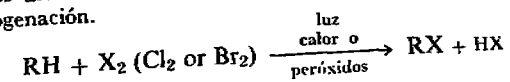
C. Reducción de halogenuros de alquilo.



Propiedades químicas.

Los alcanos son inertes a la mayoría de los reactivos.

Halogenación.



La facilidad con la cual se substituyen los hidrógenos por radicales libres en la siguiente orden: terciarios > secundarios > primarios

United States Patent [19]
Olah

[11] **Patent Number:** 4,465,893
[45] **Date of Patent:** * Aug. 14, 1984

- [54] **OXIDATIVE CONDENSATION OF
NATURAL GAS OR METHANE INTO
GASOLINE RANGE HYDROCARBONS**
- [76] **Inventor:** George A. Olah, 2252 Gloaming
Way, Beverly Hills, Calif. 90210
- [*] **Notice:** The portion of the term of this patent
subsequent to May 8, 2001 has been
disclaimed.

[21] **Appl. No.:** 410,131

[22] **Filed:** Aug. 25, 1982

[51] **Int. Cl.³** C07C 3/44

[52] **U.S. Cl.** 585/709; 585/400;
585/500; 585/700; 585/723; 585/732; 585/943;
502/224

[58] **Field of Search** 585/415, 942, 945, 709,
585/711, 717, 721, 723, 724, 730, 732; 502/224

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Primary Examiner—Delbert E. Gantz

Assistant Examiner—A. Pal

Attorney, Agent, or Firm—Pennie & Edmonds

[57] **ABSTRACT**

This invention relates to a new process for the direct
conversion of natural gas or methane into gasoline
range hydrocarbons (i.e., synthetic transportation fuels
or lower olefins) via catalytic condensation using super-
acid catalysts.

13 Claims, No Drawings

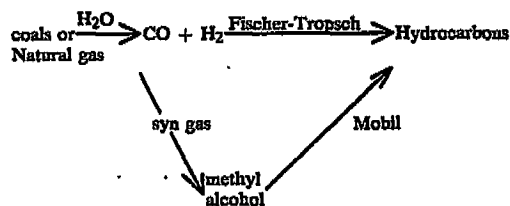
OXIDATIVE CONDENSATION OF NATURAL GAS OR METHANE INTO GASOLINE RANGE HYDROCARBONS

TECHNICAL FIELD

This invention relates to the direct conversion of natural gas or methane into gasoline-range hydrocarbons (i.e., synthetic transportation fuels or lower olefins) via catalytic condensation using superacid catalysts.

BACKGROUND ART

The present state of art for production of synthetic fuels from either coal or natural gas (the two major possible raw materials) involves initial production of synthesis gas which is then either converted directly to hydrocarbons (Fischer-Tropsch) or converted first to methyl alcohol, which subsequently is converted into hydrocarbons (Mobil process):



The Fischer-Tropsch process, although proven commercially, is not the most economically desirable process for the future due to its two very energetic steps and unsuitable product composition. The Mobil process is capable of producing gasoline-range hydrocarbons and aromatics relatively free of heavies, but suffers from the disadvantageous economics of first producing synthesis gas, which is then converted into methyl alcohol, which in turn is converted into hydrocarbons.

My discovery follows an independent and new route by utilizing methane (or natural gas) as the basic raw material. Methane as natural gas or even a biological "deep methane" is expected to be available well into the 2000's, and, if not utilized exclusively as an energy source but rather for transportation fuels and as a chemical raw material source, could last much longer. Furthermore, coal can be readily converted into methane by methanation or by in-situ gasification, thus avoiding difficulties in mining and transporting coal. Further, alternate sources of methane, such as the biological conversion of biomass (sewage recycling, utilization of plant life on land and sea [algae or kelp farming of the sea] with subsequent off shore conversion allowing the piping of methane to land), are becoming available. If in the future as cheaper atomic or fusion energy becomes available, during off-peak periods, these plants could become producers of aluminum carbide which, upon hydrolysis, gives methane (with ethane and ethylene as by-products.) The conversion of methane to higher hydrocarbons thus represents a viable new alternative to synthetic hydrocarbon processes.

The oligocondensation of methane was discovered by Olah et al., *Journal of the American Chemical Society*, 90, 2726 (1968), using exceedingly strong acid systems, the so-called "superacids", comprising a mixture of fluorosulfuric acid and antimony pentafluoride ("magic acid"), a mixture of hydrogen fluoride and antimony pentafluoride, or related superacids. Superacids have a

Hammett acidity function H_0 less than $-11.9H_0$, the value for 100 percent sulfuric acid. However, yields were extremely low and the superacid was reductively depleted, rendering the process impractical on a commercial scale.

Alkane-alkene condensations (alkylations) such as that of isobutane with isobutylene to produce C_8 alkylate is well known in the petrochemical industry. Olah reported first the alkylation of alkanes with alkyl cations, generated in superacidic media [*J. Am. Chem. Soc.*, 95, 4939-4952 (1973)].

The condensation (polymerization) of methane and olefins represents a special problem and for a long time, methane was considered to be inert to usual acid catalyzed electrophilic reactions. The work of Olah on the superacid catalyzed reactivity of methanes opened up the possibility for such reactions. D. T. Roberts, Jr. and L. E. Calihan [*J. Macromol. Sci.-Chem.*, A7 (8) pp. 1641-1646 (1973)] reported that mixtures of methane and olefins (ethylene, propylene, etc.) polymerized in an autoclave at room temperature over a liquid magic acid (HSO_3F/SbF_5) catalyst to give oily oligomers with molecular weight of 100 to 700. Conversions were low (in the case of methane and ethylene, 5%) and under the used liquid phase conditions with long contact times (generally 24 hours) the olefin itself tended to polymerize on its own. Subsequently using another liquid superacid catalyst, hydrogen fluoride-tantalum pentafluoride, Siskin carried out the alkylation of methane with ethylene in a pressurized flow system [*J. Am. Chem. Soc.*, 98, 5413 (1976)]. No yields or conversions were given and again the liquid phase reaction conditions were considered to substantially limit practical application of the reaction.

DESCRIPTION OF THE INVENTION

In sharp contrast to previous practice, I have now found a practical way to convert methane into gasoline-range hydrocarbons (synthetic transportation fuels) by condensing a gaseous feed comprising methane or natural gas in the presence of a solid or supported superacid.

The condensation of methane into higher hydrocarbons must overcome the unfavorable endothermic thermodynamics of such individual steps as noted below:



In order to overcome this difficulty, it is advantageous to oxidatively remove hydrogen. The removal of hydrogen has now been discovered to be possible in two ways.

In one embodiment of the invention higher hydrocarbons are produced when natural gas or methane is condensed in a single step in the presence of a suitable oxidant over the solid or supported superacid catalyst.

In an alternative embodiment of the invention methane or natural gas is condensed in admixture with at least one lower olefin in the C_2 to C_4 range and/or with acetylene, in the presence of the solid or supported superacid catalyst. Such admixtures are readily obtained for instance by the dehydrogenation of natural gas to a mixture of methane and lower olefins, or by the thermal treatment of natural gas to form a mixture of methane and acetylene.

The useful catalysts can be selected from higher valency Lewis Acid halides of metals of Groups IV, V and VI of the Periodic Table such as tantalum pentaflu-

oride, niobium pentafluoride, antimony pentafluoride and the like, supported on a suitable chalconite carrier, preferentially in its fluorinated form such as fluorinated alumina, or the like, or on a graphite, fluorinated graphite or aluminum trifluoride carrier.

As noted in Olah, G. A. "Friedel-Crafts Chemistry," N.Y., Wiley-Interscience, 1973. p. 343-344, the elements of Group VIA such as oxygen, sulfur, selenium or tellurium, have been called "chalcogens", and compounds containing these elements are called "chalconites", "chalcogenides" or "chalcides." A variety of solid oxides and sulfides, especially those comprising alumina, and mixtures of alumina, either natural or synthetic, in which other oxides such as chromia, magnesia, molybdena, thoria, tungstic oxide, zirconia, etc., may also be present, as well as sulfides of molybdenum are useful chalcide carriers. Many naturally occurring compositions exist for use as the carrier including: bauxite, fluorin, Georgia clay, and other natural aluminosilicates.

Synthetic chalcides, other than those of the silica-alumina type, representative of the chalcide carriers are: BeO, Cr₂O₃, P₂O₅, ThO₂, TiO₂, Al₂(SO₄)₃ (which may be regarded as Al₂O₃·3SO₃), Al₂O₃·Cr₂O₃, Al₂O₃·Fe₂O₃, Al₂O₃·CoO, Al₂O₃·MnO, Al₂O₃·V₂O₅, Al₂O₃·Mo₂O₃, Cr₂O₃·Fe₂O₃, MoS₂, and MoS₃.

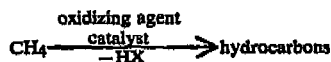
The chalcide supports should be physically and chemically stable. Under the reaction conditions, they are generally catalytically active at only higher temperatures, as their acidity is not great enough to lead them to form stable complexes with unsaturated compounds, as do the aluminum halides, for example.

Useful catalysts can also be selected from superacidic conjugated acids composed of a strong Bronsted acid such as hydrogen fluoride, fluorosulfuric acid, perfluoroalkane-sulfonic acids of 1 to 18 carbon atom length, supported on a suitable solid carrier, or polymeric perfluorinated acids such as Nafion-H or copolymers of perfluorovinyl perfluorinated polymeric resin-sulfonic acids and the like, in conjunction with a suitable Lewis Acid fluoride, such as those of the metals of Groups IV, V and VI of the Periodic Table.

The solid or supported solid catalysts are used at temperatures between about 15° and 250° C. and pressures of about 1 to 150 or more atmospheres. The feed comprises methane alone, or mixtures which generally contain a substantial excess of methane, in mole ratios of 6 to 12:1 to olefins and/or acetylene, readily obtainable from pretreatment of natural gas by catalytic dehydrogenation or thermal reaction.

These condensations generally produce alkane mixtures, as well as cycloalkanes and aromatics of less than 12 carbons, but not olefins.

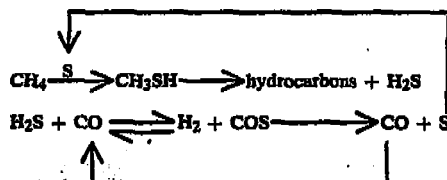
The first method involves the oxidative condensation of methane, in which an oxidizing agent, such as air, oxygen, oxygen-ozone mixture, sulfur, selenium, sulfur trioxide, nitrogen oxides, halogens (fluorine, chlorine, bromine, iodine) is utilized to remove hydrogen as noted below.



Oxidative condensation in the presence of air or oxygen gives water as by-product. Recovery of hydrogen is thus not feasible.

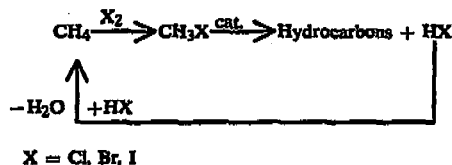
The oxidative condensation of methane with sulfur gives H₂S as a by-product. It can be readily oxidized to

recover sulfur or, alternatively, it was discovered that by combining a CO shift reaction over a supported molybdenum sulfide catalyst with catalytic or thermal decarbonylation of COS, it is possible to obtain hydrogen and regenerate sulfur, thus allowing the following condensation:



to proceed to hydrocarbons and hydrogen. This approach allows a methane condensation with the recovery of hydrogen, or is also applicable to hydrogen production from refinery gases, sour gas wells or coal desulfurization.

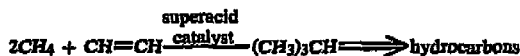
The oxidative condensation of methane can also be carried out with halogens as the oxidizing agents. Methane can be chlorinatively (brominatively, iodinatively) condensed under the reaction conditions. Initially, methyl chloride, bromide, or iodide are formed (or methyl fluoride, if the halogenation is carried out in the presence of HF) which are subsequently readily condensed into higher hydrocarbons. HCl, HBr or HI can be recycled via oxyhalogenation, whereas HF is reusable as such. The condensation reaction is preferably carried out at a temperature of about 50° to 250° C. and at a pressure of about 1 to 50 atmospheres.



The second method involves the dehydration of natural gas to a mixture of methane and lower olefins (ethylene, with some propylene and butenes) or, alternatively, its thermal treatment to form acetylene, (as well as ethylene) and condensing these mixtures in the presence of aforementioned solid superacid catalysts to hydrocarbons in the gasoline-range:



R = H, CH₃CH₂H₃
or,



As lower olefins readily undergo themselves acid catalyzed condensations, their reactions with methane must be carried out under conditions where these self condensations can be minimized. This can be achieved utilizing a suitable excess of methane and preferentially premixing anhydrous hydrogen fluoride with the olefins which intermediately form alkyl fluorides, regenerating hydrogen fluoride in the alkylation reaction



Illustrative of the invention are the following examples, set forth for the purpose of illustration only and not to be construed as limiting the scope of the invention in any matter. In the related Tables where product compositions are given, they have been normalized, even if not stated, to provide a total of 100% conversion, excluding unreacted methane which can be recycled.

EXAMPLE 1

Natural gas containing about 82% methane and 18% ethane, with some propane and butane, is subjected to conventional catalytic dehydrogenation (cracking), yielding, in addition to unreacted methane, an ethylene-propylene containing feed which after drying can be utilized directly in the condensation reaction. The obtained methane-ethylene feed (in about 90:10 ratio) containing some ethane, propylene, butylenes, which do not need to be separated, is reacted over a tantalum pentafluoride catalyst supported on fluoridated alumina (10% per weight), at a temperature of 70° C. in a continuous flow reactor. A 38% conversion per pass (based on reacted ethylene) is obtained with the following composition:

Product composition	(%) ^a
C ₂ H ₆	13.2
C ₃ H ₈	13.8
i-C ₄ H ₁₀	48.6
n-C ₄ H ₁₀	6.5
i-C ₅ H ₁₂	12.7
n-C ₅ H ₁₂	5.3

^amethane excluded and normalized to 100%

EXAMPLE 2

A feed mixture consisting of about 88% methane and 10% acetylene was treated under the conditions of Example 1 over the supported tantalum pentafluoride at 70° C. in the continuous flow reactor. A 78% conversion per pass (based on feed acetylene) was obtained with the following product distribution:

Product distribution	(%) ^a
C ₂ H ₆	3.7
C ₃ H ₈	6.1
i-C ₄ H ₁₀	84.2
n-C ₄ H ₁₀	<1
i-C ₅ H ₁₂	5.0
n-C ₅ H ₁₂	<1

EXAMPLE 3

Under the conditions of Example 2, a feed mixture consisting of about 80% methane, 10% ethylene and 10% acetylene was passed through the supported tantalum pentafluoride catalyst at 70° C. A 68% conversion per pass was obtained with the following product composition:

Product composition	(%) ^a
ethane	22.5
propane	1.8
butanes	14.1
pentanes	39.6
hexanes	22.0

EXAMPLE 4

A 9:1 natural gas (consisting of about 90% methane and 10% ethane)-oxygen mixture was reacted at a pressure of 65 atm. at 120° C. over a 20% antimony pentafluoride deposited on fluorinated graphite. A 13% conversion was obtained. The hydrocarbon product contained 21 to 27% ethylene, 6 to 8% propane, 31-40% butanes, 11-16% pentanes, with the balance being oxygenated products.

EXAMPLE 5

Methane was reacted in the presence of sulfur in the ratio of 5:1 in the presence of the tantalum pentafluoride catalyst containing HF at 270° C. in a stainless steel pressure reactor. A 2 to 10% conversion to condensed saturated hydrocarbons is achieved depending on reaction time (1 to 24 hrs) with the following product composition.

Product composition	(%) ^a
ethane	38-50
propane	5-8
butanes	40-49
pentanes	5-15

EXAMPLE 6

Methane was reacted in the presence of sulfur in a ratio of 5:1 in the presence of antimony pentafluoride catalyst at 200° C. as in Example 5. A 3 to 15% conversion with similar produce composition was obtained.

EXAMPLE 7

Methane was reacted in the presence of selenium in a ratio of 5:1 in the presence of tantalum pentafluoride catalysts at 200° C. in a stainless steel pressure autoclave for six hours. A 3 to 16% conversion to condensed saturated hydrocarbons is achieved with the following typical product composition:

Product composition	(%) ^a
ethane	18-34
propane	2-5
butanes	34-48
pentanes	11-23
hexanes	6-19

EXAMPLE 8

A 2:1 methane-chlorine mixture was reacted over a perfluorinated resinsulfonic acid (Nafion-H) catalyst complexed with 20% tantalum pentafluoride at 185° C. in the previously utilized continuous flow reactor. 40% per pass conversion gave the following product composition:

Product composition	(%) ^a
methyl chloride	2
methylene chloride	7
ethane	3
ethyl chloride	40
isobutane	48

EXAMPLE 9

A 2:1 methane-chlorine mixture was reacted over a catalyst prepared by intercalating (immobilizing) 30% antimony pentafluoride onto graphite, at 120° C. Typical per pass conversions were 32% with product composition of

Product composition	(%) ^a
methyl chloride	37-38
ethyl chloride	1-4
methylene chloride	9-14
isobutane	25-48

EXAMPLE 10

In a pressure reactor, methane was reacted over a graphite catalyst intercalated with 30% antimony pentafluoride at 20° C. and 140 psi pressure. The reactor was initiated with anhydrous HF and a halogen (fluorine, chlorine). Initial methane conversion was 15 to 29% with the following typical hydrocarbon product composition (excluding halomethanes):

Product composition	(%) ^a
ethane	8-23
propane	3-8
butanes	32-48
pentanes	11-28
hexanes	6-15

Conversion decreases with time as activity decreases during the reaction. It can, however, be restored by treating the system again with anhydrous hydrogen fluoride containing fluorine or chlorine as the oxidizing agent. The reaction is advantageously carried out using alternating parallel reactors, in one of which the reaction is carried out, while in the other system is regenerated.

EXAMPLE 11

Methane was reacted over a catalyst, which was 20% tantalum pentafluoride supported on anhydrous aluminum fluoride, in a pressure reactor at 20° C. and 140 psi. The reaction is initiated with anhydrous hydrogen fluoride and a halogen (fluorine or chlorine). The reaction was carried out and the system reactivated as in Example 10. Initial methane conversion was 12 to 19% with the following typical hydrocarbons product composition (excluding halomethanes):

Product composition	(%) ^a
ethane	8-19
propane	1-5
butanes	46-58
pentanes	12-27
hexanes	5-17

EXAMPLE 12

Methane was reacted over a solid, superacidic catalyst, prepared by intercalating graphite with 30% anti-

mony pentafluoride, with ethylene in the presence of excess hydrogen fluoride in a manner that ethylene is first contacted with hydrogen fluoride converting it into ethyl fluoride, thus avoiding presence of excess free ethylene. This can be achieved under conditions of Example 10 utilizing alternating parallel reactors. Typical hydrocarbon product compositions are:

Product composition	(%) ^a
ethane	10-15
propane	2-8
butanes	41-48
pentanes	13-21
hexanes	10-18

I claim:

1. A process for the heterogeneous gas-phase conversion of methane into gasoline-range hydrocarbons by condensing a gaseous feed comprising methane or natural gas in the presence of a solid superacid catalyst.

2. A process according to claim 1 wherein the gaseous feed is condensed in the presence of an oxidizing agent selected from air, oxygen, oxygen-ozone mixtures, sulfur, selenium, sulfur trioxide, nitrogen oxides and halogens.

3. A process according to claim 1 wherein the solid superacid catalyst is selected from higher valency Lewis Acid halides of metals of groups IV, V or VI of the Periodic Table, supported on a carrier.

4. A process according to claim 3 wherein the higher valency Lewis Acid halide is selected from tantalum pentafluoride, niobium pentafluoride and antimony pentafluoride.

5. A process according to claim 3 wherein the carrier is a chalconite, graphite, fluorinated graphite or aluminum fluoride.

6. A process according to claim 5, wherein the chalconite carrier is fluoridated.

7. A process according to claim 1 wherein the solid superacid catalyst is composed of a strong Bronsted acid component selected from hydrogen fluoride, fluorosulfuric acid, perfluoroalkanesulfonic acids of 1 to 18 carbon atoms deposited on a suitable carrier, perfluorinated polymeric resinsulfonic acids copolymers of perfluorovinylsulfonic acid and tetrafluoroethylene or trifluorochloroethylene complexed with a Lewis Acid fluoride of metal of groups IV, V or VI of the Periodic Table.

8. A process according to claim 1 wherein the solid superacid catalyst is antimony pentafluoride deposited on graphite or fluorinated graphite.

9. A process according to claim 1 wherein the solid superacid catalyst is tantalum pentafluoride deposited on aluminum trifluoride, fluoridated alumina, graphite or fluorinated graphite.

10. A process according to claim 1 wherein the gaseous feed is condensed at a temperature between about 15 and 250 degrees centigrade and a pressure of about 1 to 150 atmospheres.

11. A process according to claim 1 wherein the gaseous feed is condensed at a temperature between about 50 and 250 degrees centigrade and a pressure of about 1 to 150 atmospheres.

12. A process according to claim 1 wherein the methane or natural gas is condensed in admixture with at least one lower olefin in the C₂ to C₄ range.

13. A process according to claim 1 wherein the methane or natural gas is condensed in admixture with acetylene.

* * * * *

United States Patent [19]

Butter et al.

[11] 3,894,107

[45] July 8, 1975

[54] **CONVERSION OF ALCOHOLS,
MERCAPTANS, SULFIDES, HALIDES
AND/OR AMINES**

[75] Inventors: **Stephen A. Butter**, East Windsor;
Anthony T. Jurewicz, Kendall Park;
Warren W. Kaeding, Westfield, all
of N.J.

[73] Assignee: **Mobil Oil Corporation**, New York,
N.Y.

[22] Filed: **Aug. 9, 1973**

[21] Appl. No.: **387,223**

[52] U.S. Cl. **260/668 R; 260/673; 260/676 R;
208/141**

[51] Int. Cl.² **C07C 15/02**

[58] Field of Search **260/668, 673, 673.3, 449 R,
260/449 M, 676 R; 48/197; 208/141**

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Primary Examiner—**C. Davis**

Attorney, Agent, or Firm—**Charles A. Huggett;**

Michael G. Gilman

[57] **ABSTRACT**

Process of converting alcohols, aliphatic mercaptans, aliphatic sulfides, aliphatic halides and/or aliphatic amines to other desirable products by contacting such with a particular type of aluminosilicate molecular sieve catalyst at elevated temperature. Products produced by such conversion vary with temperature, with conversion to aromatic rings and substituted aromatic rings predominating at higher temperatures of about 300° to 500°C. The catalyst is a zeolite having a high silica to alumina ratio of at least about 12 and a constraint index of about 1 to 12. It also preferably has a crystal density in the hydrogen form of not substantially less than about 1.6.

21 Claims, No Drawings

CONVERSION OF ALCOHOLS, MERCAPTANS, SULFIDES, HALIDES AND/OR AMINES

This invention relates to conversion of certain organic compounds to other, more complicated organic compounds.

There has recently been discovered a certain novel class of crystalline aluminosilicate zeolites which have been shown to have unusual properties. These catalysts induce profound transformations of aliphatic hydrocarbons to aromatic hydrocarbons in commercially desirable yields. Although they have unusually low alumina contents, i.e. high silica to alumina ratios, they are very active even when the silica to alumina ratio exceeds 30. The activity is surprising since the alumina in the zeolite framework is believed responsible for catalytic activity. These catalysts retain their crystallinity for long periods in spite of the presence of steam at high temperature which induces irreversible collapse of the framework of other zeolites, e.g. of the X and A type. Furthermore, carbonaceous deposits, when formed, may be removed by burning at higher than usual temperatures to restore activity.

An important characteristic of the crystal structure of this class of zeolites is that it provides constrained access to, and egress from, this intracrystalline free space by virtue of having a pore dimension greater than about 5 Angstroms and pore windows of about a size such as would be provided by 10-membered rings of oxygen atoms. It is to be understood, of course, that these rings are those formed by the regular disposition of the tetrahedra making up the anionic framework of the crystalline aluminosilicate, the oxygen atoms themselves being bonded to the silicon or aluminum atoms at the centers of the tetrahedra. Briefly, the preferred type catalyst useful in this invention possess, in combination: a silica to alumina ratio of at least about 12; and a structure providing constrained access to the crystalline free space.

The silica to alumina ratio referred to may be determined by conventional analysis. This ratio is meant to represent, as closely as possible, the ratio in the rigid anionic framework of the zeolite crystal and to exclude aluminum in the binder or in cationic form within the channels. Although catalysts with a silica to alumina ratio of at least 12 are useful, it is preferred to use catalysts having higher ratios of at least about 30. Such catalysts, after activation, acquire an intracrystalline sorption capacity for normal hexane which is greater than that for water, i.e. they exhibit "hydrophobic" properties. It is believed that this hydrophobic character is advantageous in the present invention.

The type zeolites useful in this invention freely sorb normal hexane and have a pore dimension greater than about 5 Angstroms. In addition, the structure must provide constrained access to larger molecules. It is sometimes possible to judge from a known crystal structure whether such constrained access exists. For example, if the only pore windows in a crystal are formed by eight-membered rings of oxygen atoms, then access to molecules of larger cross-section than normal hexane is excluded and the zeolite is not of the desired type. Windows of 10-membered rings are preferred, although excessive puckering or pore blockage may render these catalysts ineffective. Twelve-membered rings do not generally appear to offer sufficient constraint to produce the advantageous conversions, although struc-

tures can be conceived, due to pore blockage or other cause, that may be operative.

Rather than attempt to judge from crystal structure whether or not a catalyst possesses the necessary constrained access, a simple determination of the "constraint index" may be made by passing continuously a mixture of equal weight of normal hexane and 3-methylpentane over a small sample, approximately 1 gram or less, of catalyst at atmospheric pressure according to the following procedure. A sample of the catalyst, in the form of pellets or extrudate, is crushed to a particle size about that of coarse sand and mounted in a glass tube. Prior to testing, the catalyst is treated with a stream of air at 1000°F for at least 15 minutes. The catalyst is then flushed with helium and the temperature adjusted between 550° and 950°F to give an overall conversion between 10 and 60%. The mixture of hydrocarbons is passed at 1 liquid hourly spaced velocity (i.e. 1 volume of hydrocarbon per volume of catalyst per hour) over the catalyst with a helium dilution to give a helium to total hydrocarbon mole ratio of 4:1. After 20 minutes on stream, a sample of the effluent is taken and analyzed, most conveniently by gas chromatography, to determine the fraction remaining unchanged for each of the two hydrocarbons.

The constraint index is calculated as follows:

$$\text{Constraint Index} = \frac{\text{Log}_{10} (\text{fraction of n-hexane remaining})}{\text{Log}_{10} (\text{fraction of 3-methylpentane remaining})}$$

The constraint index approximates the ratio of the cracking rate constants for the two hydrocarbons. Catalysts suitable for the present invention are those having a constraint index from 1.0 to 12.0, preferably 2.0 to 7.0.

The class of zeolites defined herein is exemplified by ZSM-5, ZSM-11, ZSM-12, ZSM-21, TEA mordenite and other similar materials. Recently issued U.S. Pat. No. 3,702,886 describing and claiming ZSM-5 is incorporated herein by reference.

ZSM-11 is more particularly described in U.S. Pat. No. 3,709,979, the entire contents of which are incorporated herein by reference.

ZSM-12 is more particularly described in West German Offenlagunschrift No. 2,213,109, the entire contents of which are incorporated herein by reference.

ZSM-21 is more particularly described in U.S. application, Ser. No. 358,192, filed May 7, 1973, now abandoned, the entire contents of which are incorporated herein by reference.

TEA mordenite is more particularly described in U.S. application Ser. No. 130,442 filed Apr. 11, 1971, the entire contents of which are incorporated herein by reference.

The specific zeolites described, when prepared in the presence of organic cations, are catalytically inactive, possibly because the intracrystalline free space is occupied by organic cations from the forming solution. They may be activated by heating in an inert atmosphere at 1000°F for 1 hour, for example, followed by base exchange with ammonium salts followed by calcination at 1000°F in air. The presence of organic cations in the forming solution may not be absolutely essential to the formation of this type zeolite; however, the presence of these cation does appear to favor the formation of this special type of zeolite. More generally, it is desir-

able to activate this type catalyst by base exchange with ammonium salts followed by calcination in air at about 1000°F for from about 15 minutes to about 24 hours.

Natural zeolites may sometimes be converted to this type zeolite catalysts by various activation procedures and other treatments such as base exchange, steaming, alumina extraction and calcination, in combinations. Natural minerals which may be so treated include ferrierite, brewsterite, stillbite, dachiardite, epistilbite, heulandite and clinoptilolite. The preferred crystalline aluminosilicates are ZSM-5, ZSM-11, ZSM-12, ZSM-21 and TEA mordenite, with ZSM-5 particularly preferred.

The catalysts of this invention may be in the hydrogen form or they may be base exchanged or impregnated to contain ammonium or a metal cation complement. It is desirable to calcine the catalyst after base exchange. The metal cations that may be present include any of the cations of the metals of Groups I through VIII of the periodic table. However, in the case of Group IA metals, the cation content should in no case be so large as to effectively inactivate the catalyst. For example, a completely sodium exchanged H-ZSM-5 is not operative in the present invention.

In a preferred aspect of this invention, the catalysts hereof are selected as those having a crystal density, in the dry hydrogen form, of not substantially below about 1.6 grams per cubic centimeter. It has been found that zeolites which satisfy all three of these criteria are most desired because they tend to maximize the production of gasoline boiling range hydrocarbon products. Therefore, the preferred catalysts of this invention are those having a constraint index as defined above of about 1 to 12, a silica to alumina ratio of at least about 12 and a dried crystal density of not less than about 1.6 grams per cubic centimeter. The dry density for known structures may be calculated from the number of silicon plus aluminum atoms per 1000 cubic Angstroms, as given, e.g. on page 11 of the article on Zeolite Structure by W. M. Meier. This paper, the entire contents of which are incorporated herein by reference, is included in "Proceedings of the Conference on Molecular Sieves, London, April 1967", published by the Society of Chemical Industry, London, 1968. When the crystal structure is unknown, the crystal framework density may be determined by classical pyknometer techniques. For example, it may be determined by immersing the dry hydrogen form of the zeolite in an organic solvent which is not sorbed by the crystal. It is possible that the unusual sustained activity and stability of this class of zeolites is associated with its high crystal anionic framework density of not less than about 1.6 grams per cubic centimeter. This high density of course must be associated with a relatively small amount of free space within the crystal, which might be expected to result in more stable structures. This free space, however, is important as the locus of catalytic activity.

A remarkable and unique attribute of this type of zeolite is their ability to convert paraffinic hydrocarbons to aromatic hydrocarbons in exceptionally fine, commercially attractive yields by simply contacting such paraffins with such catalyst at high temperatures of about 800° to 1500°F and low space velocities of about 1 to 15 WHSV. This type of zeolite seems to exert little or no action upon aromatic rings present in the feed to such process or formed in such process from the point of view of destroying (cracking) such rings. It does

however have the ability, with or without the presence of a special hydrogen transfer functionality and with or without the presence of added hydrogen in the reaction mixture, to cause paraffinic fragments, which presumably have been cracked from paraffinic feed components, to alkylate aromatic rings at somewhat lower temperatures of up to about 800° to 1000°F. It appears that the operative ranges for alkylation and formation of new aromatic rings overlap but that the optimum ranges are distinct, aromatization being at a higher temperature. The exact mechanisms for these catalytic functions are not fully known or completely understood.

It is generally believed by those knowledgeable in the crystalline zeolite art, that contact of a zeolite with steam is deleterious to the catalytic properties thereof and that increase in pressure, temperature and/or time of contact increases the adverse effects on the catalyst. While this type zeolite is substantially more steam stable than other zeolites, it has been found to be possible to reduce or eliminate its aromatization catalytic activity. Aromatization of aliphatic hydrocarbons as described in U.S. Pat. application Ser. No. 253,942, filed May 17, 1972, now U.S. Pat. No. 3,756,942, has been attempted using this type of aluminosilicate which had previously been severely steam treated. It was found to be substantially impossible to aromatize paraffinic hydrocarbons as set forth in such patent application with such deactivated catalyst.

It is known that many acid catalysts are capable of assisting in the dehydration of alcohols to ethers and/or olefins. In the case of methanol, such dehydration reactions have proceeded to dimethyl ether as the principal product. In all or at least most of these prior processes, the dehydrated product had a longest carbon atom chain length which was not longer than the longest carbon atom chain length of the reactant. For the most part, such dehydration reactions did not produce products having a molecular weight in any given hydrocarbon portion which was higher than the molecular weight of the hydrocarbon portion of the reactant.

Alkanols of 2 or more carbon atoms were generally dehydrated to their corresponding olefins or to their corresponding ethers e.g. ethanol to ethylene and/or diethyl ether or isopropanol to propylene or diisopropyl ether. Methanol, on the other hand, represented a special case in that it has only 1 carbon atom and therefore could not be dehydrated to an olefin. Methanol dehydrated to dimethyl ether with the usual prior art dehydration process and catalyst.

It is an object of this invention to provide a novel process for converting various aliphatic hetero compounds of the R-X type to other valuable products, particularly higher hydrocarbons.

It is another object of this invention to convert aliphatic alcohols, halides, mercaptans, sulfides and/or amines to their corresponding ethers or analogous compounds in a very efficient manner.

It is a further object of this invention to convert alcohols to their corresponding olefins in a very efficient manner.

It is still another object of this invention to provide a novel process for converting alcohols and/or other aliphatic hetero atom containing compounds to products having a greater number of carbon atoms in a continuous hydrocarbon portion of the product than in the feed.

Other and additional objects of this invention will become apparent from a consideration of this entire specification including the claims hereof.

In accord with and fulfilling these objects, one aspect of this invention lies in the discovery that hetero organic compounds of the R-X type are convertible to other organic chemical products, notably aromatic hydrocarbons, by contacting such compounds with an aluminosilicate molecular sieve zeolite having a silica to alumina ratio of at least about 12 and a constraint index of about 1 to 12 at elevated temperatures up to about 1000°F, preferably about 500° to 850°F, a pressure of about atmospheric to 1000 psig, preferably 0.5 to 75 psig, a space velocity of about 0.5 to 50 WHSV in the presence or absence of added hydrogen.

The reactants useful in this invention have been designated to be of the R-X type where R stands for an aliphatic hydrocarbon moiety, X stands for a hetero atom such as sulfur, nitrogen, halogen or oxygen. The types of reactant compounds found to be useful in this invention are alcohols, mercaptans, sulfides, halides and amines. The aliphatic hydrocarbon moiety suitably has up to about 8 carbon atoms therein, preferably about 1 to 4 carbon atoms.

According to this invention, the reactive feed to the process hereof is critically defined as consisting essentially of lower aliphatic organic hetero compounds. This feed definition is specifically intended to distinguish from feeds used in alkylation reactions catalyzed by ZSM-5 type of synthetic aluminosilicate molecular sieve. In such alkylation reactions, which are considered to be the invention of other than the instant applicants, alkylating moieties, which may be alcohols and/or other compounds, are reacted with preformed and co-reacted aromatic moieties. In other words, alkylation requires the co-feeding of aromatic moieties and alkylating moieties such as alcohols. The instant process is to be distinguished in that it does not require or desire the co-feeding of preformed aromatic moieties.

In this regard two very important points must be emphasized: In the first place, it has now been discovered that the presence of preformed aromatic moieties as a co-feed to this reaction does not negate the aromatization conversion of the reactants designated above as the feed to the instant process; In the second place, new aromatic moieties created from the reactants hereof by the conversion process of this invention are themselves sometimes alkylated under these processing conditions by the alkylating action of the alcohol or other reactant and/or one or more intermediate moiety formed in the reaction being undergone. The process of this invention must therefore be distinguished from an alkylation reaction per se carried out with the same catalyst and under co-extensive reaction conditions.

In its broadest aspects, this invention envisions a process for condensing certain feed materials and growing the products thus formed into significantly different chemical moieties. The commercially most important aspect of this invention may be the conversion of lower alcohols to olefinic and/or aromatic hydrocarbon compounds as aforesaid. However, as an adjunct to this conversion, the reaction can be carried out under different conditions but with the same catalyst to produce somewhat different chemical values. For example, lower alkyl alcohols can be converted to lower alkyl ethers when this process is operated at low temperatures. At intermediate temperatures and severities ole-

fins of various chain length are formed from alcohol reactants.

While at first glance, the formation of olefins by contacting alcohols or other compounds with hetero atoms with an acidic zeolite at elevated temperatures might not seem too surprising, it must be pointed out that the olefins formed do not necessarily conform to the carbon configuration of the reactant. While simple "dehydration" to form a corresponding olefin may take place to a greater or lesser extent depending upon reaction conditions, the produced olefin often does have a longer carbon to carbon chain than did the reacting moiety from which it was derived. It is even more surprising that one can produce olefins such as ethylene and propylene from methanol, that is effectively a one carbon atom reactant.

According to this invention aromatics are produced from lower aliphatic hetero compounds, particularly alcohols, at about 300° to 500°C, 0.5 to 75 psig and 0.5 to 50 WHSV. Reducing the severity of the reaction conditions at about 350 to 500°F, 0.5 to 2.0 psig and 1 to 5 WHSV, causes the reaction to proceed toward ethers as the predominant product.

Suitable reactants for use in this invention are lower aliphatic alcohols, preferably lower straight or branched chain alkanols; such as methanol, ethanol, iso and normal propanol, butanols, pentanols, hexanols, cyclo hexanol heptanols, octanols such as 2 - ethyl hexanol and isooctanol, their unsaturated counterparts, or mixtures thereof such as oxoalcohol mixtures. Nitrogen, halogen and sulfur analogues thereof such as methyl mercaptan, methyl amine, ethyl mercaptan, n-butyl amine, cyclohexyl amine, methyl sulfide, etc., as well as mixtures thereof; and mixtures of such alcohols and other materials as aforesaid. These reactants may be used as pure or impure chemical streams including the unresolved product of upstream processing intended to produce such alcohols or other hetero aliphatic compounds as a predominant product.

It is within the scope of this invention to convert the alcohol or other noted feed compounds as pure individual compounds or as admixtures of normal chemical purity. It is also within the scope of this invention to feed such individual reactants in admixture with other different materials. These other feed materials may be reactive or inert under the conditions of this process. Their presence or absence is not a part of this invention. Thus, for example, it is the subject of concurrently filed patent applications of different inventors to convert carbonyl containing compounds or alkoxy type compounds to more complex compounds under substantially the same conditions as are set forth herein. The co-feeding and co-reaction of the feeds, or one of them, set forth in said other patent application with the feeds of this application, including possible interaction of these feeds and/or intermediates produced therefrom is not considered to be outside the scope of either this or that patent application. Rather, such is considered to be within the scope of each respective application as to that portion of the feed related to that application.

It is surprising and indeed quite unexpected that this process should work as well as it does in view of the fact that it produces 1 mole of steam, ammonia, hydrogen sulfide, hydrogen halide, etc. per mole of reactant converted to hydrocarbon product. Since the presence of steam and other similar molecules at elevated tempera-

tures is known to adversely affect the catalytic activity of most zeolite catalysts in general, and it is known that steam can deactivate the instant type of aluminosilicate for hexane aromatization reactions, the fact that the instant described aromatization of hetero atom containing compounds not only takes place in this atmosphere but seems not to be adversely affected by this environment, in which it is necessarily carried out, is surprising.

An additional unexpected aspect of this invention resides in the discovery that, although it is usual and common for conversion reactions carried out in the presence of and in contact with zeolite catalysts in general

favor ether formation, intermediate temperatures favor olefin formation and higher temperatures, which are still generally lower than hydrocarbon aromatization temperatures, favor aromatization.

The following Examples are illustrative of this invention without being limiting on the scope thereof.

EXAMPLES 1-6

In these Examples, methanol was contacted with 10 parts by weight of H ZSM-5 at low space velocities and varying temperatures. The products produced from methanol conversion were determined. All data from these runs are set forth in the following Table 1.

TABLE 1

Example No.	1	2	3	4	5	6
Temp. (°F)	297	405	518	630	710	813
Feed (parts by weight per hr.)	8.4	7.64	7.13	6.34	6.57	7.84
Methanol conversion (%)	16.9	75	64	100	100	100
WHSV	0.84	0.76	0.71	0.63	0.66	0.78
Product Selectivity (%)						
Dimethyl ether	99	99	90	0	0	0
Aliphatic hydrocarbons	0	0	10	60	55	54
Aromatic hydrocarbons	0	0	0	40	45	46

and ZSM-5 type of aluminosilicate zeolite catalyst in particular to form coke and deposit such on the zeolite catalyst whereby gradually deactivating the catalyst, the coke make deposited on this type of catalyst in the process of this invention is exceedingly small, much smaller than that encountered when subjecting corresponding hydrocarbon feeds to the same conversion conditions.

It is interesting to note that while aromatization of hydrocarbons, even unsaturated hydrocarbons, is initiated to a meaningful extent at about 650°F and is maximized from a commercially desirable product distribution point of view at about 1000°F, aromatization of lower alcohols or other R-X materials to generally the same commercially acceptable product distribution initiates at about 500°F and is maximized at about 750°F. Contacting aliphatic hydrocarbons with this type of aluminosilicate zeolites in the same temperature and other operating condition ranges as set forth above according to this invention does not induce significant production of new aromatic rings but more usually tends to alkylate preformed, co-fed aromatic ring moieties. In this regard it should be understood that there is not a clear line of demarcation between operation

EXAMPLES 7 and 8

In these Examples, ethanol was contacted with 10 parts by weight of H ZSM-5 at 1 to 2 WHSV and different temperatures. The products produced from ethanol were determined.

Example No.	7	8
Temp. (°F)	585	690
Feed (parts by weight per hr.)	9.65	10.05
Products (major)	predominantly aliphatic hydrocarbons in the C ₃ range	similar to 7 with higher aromatic content

EXAMPLES 9-17

In a manner similar to that referred to above in Examples 1 through 8, other reactants were converted in contact with H ZSM-5 as set forth below.

TABLE 2

Example Nos.	9	10	11	12
Reactant	Isopropanol	2-ethylhexanol	Mixed oxo-alcohols	Mixed pentanols
Temperature °F	350	700	800	800
WHSV	1.5	0.5	0.5	0.5
Reactant Conversion %	62	90	99	99
Products Formed	10% Isopropyl ether (a) 90% Propylene (a) hydrocarbons Water	40-50% aromatic hydrocarbons 40-50% aliphatic hydrocarbons Water	40-50% aromatic hydrocarbons 40-50% aliphatic hydrocarbons Water	49-50% aromatic hydrocarbons 40-50% aliphatic hydrocarbons Water

NOTE: (Water) is a product. The organic portion (a) totals up to 100% of the organic product.
(a) organic product

conditions which induce alkylation as opposed to aromatization of fed aliphatic hydrocarbons according to previously described processes. Similarly, there is not a clear line of demarcation in product distribution as a function of temperature in the process of this invention. It can be said in general that lower temperatures

EXAMPLES 18-24

The following Examples illustrate the conversion of mixtures of methanol and propylene, according to this invention, upon contact with 8.35 parts by weight of H ZSM-5 at the conditions shown.

TABLE 3

Example No.	18	19	20	21	22	23	24
Temp. (°F)	320	378	252	299	356	392	472
Propylene feed (in moles/min.)	2.5	2.5	2.5	2.5	2.5	2.5	2.5
Methanol feed (pts./min.)	4.1	4.2	4.0	1.9	1.8	1.7	1.7
Methanol conversion %	40	22	low	4	10	19	high
Product Selectivity %							
Dimethyl ether	82.5	86	0	82	75	79	0
Methyl isopropyl ether	17.5	14	100	18	25	21	0
Diisopropyl ether			Negligible				
Aliphatic hydrocarbon	—	—	—	—	—	—	60
Aromatic hydrocarbon	—	—	—	—	—	—	40

EXAMPLES 25-26

The following Table 4 reports the results of converting hetero atom containing aliphatics (other than oxygen) to higher hydrocarbons by contact with a zeolite catalyst according to this invention.

TABLE 4

Example No.	25	26
Feed	Methyl Mercaptan	Tri-n-butyl Amine
Temperature °F	550	500
WHSV	1.4	2.3
Aliph	—	.24
WT %		
H ₂	—	0
CO	0	0
CO ₂	0	0
CH ₄	19.53	.98
C ₂ H ₆	3.23	4.38
C ₂ H ₄	1.00	5.34
C ₂ H ₂	3.23	1.54
C ₃ H ₈	.65	17.93
IC ₃ H ₁₀	.23	.31
nC ₃ H ₁₀	.23	1.70
C ₃ H ₆	.23	39.56
C ₃ H ₄	0	4.87
C ₄	0	8.78
C ₅	0	3.42
C ₇ +	0	2.47
Wt. %		
CH ₃ SH	3.9	—
(CH ₃) ₂ S	3.5	—
H ₂ S	50.6	—
CS ₂	8.4	—
Arom.		
Wt. %		
Benzene	2.10	.59
Toluene	1.61	.80
Xylenes	.32	1.55
ArC ₃	.05	1.44
ArC ₁₀	.97	1.85
Aliphatic Wt. %	31.40	93.37
Aromatic Wt. %	1.83	6.63
S-Compos Wt. %	15.8	—
H ₂ S Wt. %	50.6	—
Conversion %	96.1	97.5
Material Bal. %		97.6

The process of this invention can be carried out in rather conventional up-flow or down-flow reactors packed with an aluminosilicate zeolite catalyst as defined herein. The zeolite catalyst alone or in a matrix suitably occupies about 75 to 95% of the reaction zone volume. It may be used in a fixed or fluidized bed arrangement. Suitable heating and/or cooling means may be employed according to conventional reaction zone temperature profiling design. The catalyst is suitably of a particle size of about 8 to 12 mesh of compacted crystal. If fluidized bed operation is undertaken, the catalyst will be necessarily be used in smaller particle size and will occupy less of the reactor volume as is well known and conventional fluidized bed practice.

Attention is directed to U.S. Pat. No. 3,036,134 issued May 22, 1962 in the name of Mattox which discloses the conversion of lower alkanols to their respective ethers at 350° to 800°F in contact with crystalline

aluminosilicate catalyst. The general and specific description of the catalyst in this reference neither includes nor suggests ZSM-5 type of zeolite. Further, it is pointed out that while the reference shows substantially complete conversion of methanol to dimethyl ether at 500°F, the catalyst of this invention causes a much lower ether production at this temperature and a much higher hydrocarbon production. Incidentally, Mattox does not appear to have produced aromatics with his process.

What is claimed is:

1. In a process of condensing an aliphatic organic compound of the formula R-X where X is at least one of halogen, oxygen, sulfur or nitrogen by contacting such with a high silica to alumina ratio crystalline aluminosilicate zeolite catalyst; the improvement which comprises: utilizing a catalyst comprising such zeolite having a silica to alumina ratio of at least about 12 and a constraint index of about 1 to 12; condensing at a temperature of about 500° to 1000°F, a pressure of about 0.5 to 1000 psig and a space velocity of about 0.5 to 50 WHSV; and converting said organic compound reactant to a product comprising a complex mixture of compounds including hydrocarbon compounds having a greater number of carbon atoms than said organic compound reactant, a higher ratio of carbon atoms to hetero atoms than said organic compound reactant and a longest carbon to carbon chain length which is longer than the longest carbon to carbon chain length of said organic compound reactant.
2. A process as claimed in claim 1 wherein said reactant hetero atom is oxygen and said aliphatic moiety has up to about 4 carbon atoms in a longest carbon to carbon chain constituent thereof.
3. A process as claimed in claim 1 wherein said reactant comprises a mixture of lower alkanols.
4. A process as claimed in claim 1 wherein said reactant comprises a lower alkanol.
5. A process as claimed in claim 1 wherein said aliphatic organic compound reactant is an alcohol having up to about 8 carbon atoms in its longest carbon to carbon chain and wherein said hydrocarbon compound products comprise a mixture of aromatic hydrocarbons.
6. A process as claimed in claim 1 wherein said product comprises C₄- and C₅-hydrocarbons.
7. A process as claimed in claim 1 carried out in contact with H-ZSM-5.
8. A process as claimed in claim 1 wherein said reactant comprises methanol.
9. A process as claimed in claim 1 wherein said reactant consists essentially of methanol.
10. A process as claimed in claim 1 wherein said zeolite has a crystal density in the hydrogen form of not

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substantially less than about 1.6 grams per cubic centimeter.

11. The conversion of lower alcohols or mixtures thereof with different materials to respectively different organic compound products, which products have respectively a higher carbon to oxygen ratio and at least the same longest carbon to carbon chain length than the reactant from which it was derived, by contacting such with a crystalline aluminosilicate molecular sieve zeolite having a silica to alumina ratio of at least about 12 and a constraint index of about 1 to 12 at an elevated temperature up to about 1000°F under such combination of temperature, pressure and space velocity as to induce said conversion.

12. In the process of condensing a lower aliphatic alcohol having 1 to 8 carbon atoms by contacting such with a crystalline aluminosilicate zeolite having a high silica to alumina ratio of at least 12 under conversion conditions to produce a product comprising water and an organic dehydration product of said alcohol; the improvement which comprises: carrying out said conversion at at least about 500°F; using as catalyst said zeolite having a crystal density of not substantially less than about 1.6 grams per cubic centimeter and a constraint index of about 1 to 12; and converting said alcohol to a product comprising mixed aliphatic and aromatic hydrocarbons.

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matic hydrocarbons.

13. The improved process claimed in claim 12 including selecting said alcohol from at least one member of the group consisting of methanol, ethanol and isopropanol; and converting such to a product comprising C₅+ aliphatic and aromatic hydrocarbons.

14. The improved process claimed in claim 12 wherein said alcohol is methanol.

15. The improved process claimed in claim 12 wherein said zeolite is a ZSM-5.

16. The improved process claimed in claim 12 wherein said zeolite is a ZSM-11.

17. The improved process claimed in claim 12 wherein said zeolite is a ZSM-12.

18. The improved process claimed in claim 12 wherein said zeolite is a ZSM-21.

19. The improved process claimed in claim 12 wherein said zeolite is a TEA Mordenite.

20. The improved process claimed in claim 12 carried out at a nominal temperature of about 750°F to convert said reactant to a product comprising aromatic hydrocarbons.

21. The improved process claimed in claim 12 including co-converting propylene with said alcohol to produce a product comprising aromatic hydrocarbons.

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PATENT SPECIFICATION

DRAWINGS ATTACHED

L104294



L104294

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Int. Cl.: —C 07 c 17/10, C 07 c 29/12

COMPLETE SPECIFICATION

Production of Lower Alkanols and Lower Alkyl Bromides

I, RALPH WILLIAM KING, a British subject, of 19, Grosvenor Place, London, S.W.1., do hereby declare the invention, for which I pray that a patent may be granted to me and the method by which it is to be performed, to be particularly described in and by the following statement:—

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This invention relates to the production of alkyl bromides and alkanols from lower alkanes including cyclo-alkanes. The invention is primarily concerned with the production of methyl and ethyl alcohols from methane and ethane, and secondary normal C_3 to C_6 alcohols e.g., isopropanol, secondary normal butanol methyl n-propyl carbinol and diethyl carbinol from the corresponding normal paraffins.

The alcohols referred to are according to the prior art produced by a variety of methods. In the case of ethyl alcohol, isopropyl alcohol and secondary normal butanol, the most widely used method is by hydration of the corresponding olefin by the use of catalysts (e.g. sulphuric acid and alumina) at moderate to high pressures, and moderately elevated temperatures.

It is an object of the invention to provide an economic process for the production of lower alkanols starting from alkanes which are relatively low cost raw materials. All the paraffin hydrocarbons concerned are found widely in nature, i.e., in natural gas and petroleum deposits, and frequently employed as fuel. The olefins on the other hand are not found in nature in significant quantities and are manufactured by special cracking operations. Because of their greater chemical reactivity than the paraffins, they are much sought after as intermediates in the manufacture of many industrial chemicals and finished products in the fields of plastics, rubber, detergents and solvents. Ethylene in particular

has assumed great importance in this connection over the past two decades, and is specially manufactured on a large industrial scale as an intermediate in the production of many products including ethanol. Ethane which is sometimes used as a feedstock in the manufacture of ethylene, and is also produced as a by-product when other feedstocks are employed, has little alternative value other than as fuel. Thus, the large price differential between ethylene and ethane provides a useful incentive for the manufacture of ethanol in particular starting from ethane as the raw material.

In other cases, such as the production of secondary normal pentanols, the corresponding paraffin (normal pentane) is sometimes employed as raw material, in a process which consists in chlorination of pentane to a mixture of amyl chlorides followed by alkaline hydrolysis of the amyl chlorides to the corresponding pentanol and sodium or other alkali metal chloride. This process involves a large usage both of chlorine and alkali — generally caustic soda—which it is a further object of the present invention to avoid.

The term "lower" as used herein to define alkanes, alkyl bromides or alkanols refers to such compounds having up to 8 carbon atoms in the molecule. Further, the alkanes, alkyl bromides and alkanols referred to herein include the cycloalkanes, cycloalkyl bromides and cycloalkanol.

Where reference is made in this specification to "alkyl bromide" this refers to the mono-bromide or mixture of mono-bromides, when such a mixture is formed.

According to the invention, a process for the production of a lower alkanol from the corresponding alkane comprises reacting an excess of the alkane with bromine at an elevated temperature to produce the correspond-

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ing alkyl bromide and hydrogen bromide, separating the alkyl bromide and subjecting it to hydrolysis at an elevated temperature with water or steam as the hydrolysing agent to produce the corresponding alkanol and hydrogen bromide, recovering the alkanol, oxidising hydrogen bromide recovered from the products of the bromination step and from the products of the hydrolysis step to produce bromine and recycling the bromine thus produced to the bromination step.

The invention also includes a process for the production of a lower alkyl bromide from the corresponding alkane which comprises reacting an excess of the alkane with bromine at an elevated temperature to produce the alkyl bromide and hydrogen bromide, separating the hydrogen bromide from the alkyl bromide, recovering the alkyl bromide, oxidising hydrogen bromide separated from the products of the bromination step to produce bromine and recycling the bromine to the bromination step.

The bromination reaction is preferably carried out with the alkane and the bromine in the vapour state, preferably in the presence of a minor proportion of water vapour. However, it is possible to effect the bromination by contacting the alkane in vapour form with a solution of bromine in aqueous hydrogen bromide.

Broadly speaking, the bromination reaction may be carried out at a temperature of 80° to 450°C. and under a pressure of from 1 to 200 atmospheres absolute. When the bromine is in vapour form and no catalyst is employed, the temperature is preferably in the range 200 to 350°C., the pressure in the range 1 to 25, more preferably 5 to 15 atmospheres absolute, and the contact time in the range 2 to 20 seconds depending on the particular alkane or mixture of alkanes employed. The temperatures and pressures preferred for the reaction are higher in the case of the lower alkanes, methane and ethane, than in the case of the higher C₃ to C₄ alkanes.

It is also possible to effect the reaction at lower temperatures, i.e., in the range 125 to 180°C. with the use of catalysts, ultra-violet light or a silent electric discharge, and in this case the bromine may be brought into contact with the alkane vapour as a solution in aqueous hydrogen bromide. A suitable catalyst for the bromination is tetraethyl lead or other catalyst generating free radicals in the reaction.

In every case an excess of alkane should be maintained in the reaction zone, preferably such that the molar ratio of alkane to bromine is in the range between 2:1 and 20:1, more preferably 3:1 and 10:1, suitably 5:1; this reduces the amount of dibromo and higher brominated products formed.

In the preferred method of procedure in which bromine is introduced as vapour into

the bromination reactor, heat is evolved and a temperature rise occurs in the reactor, which temperature rise depends on the alkane used and the excess of alkane over bromine in the reactor feed. Conditions are chosen so that substantially complete reaction of the bromine takes place and only traces of unreacted bromine leave in the effluent from the reactor. Generally speaking, the reactor is operated adiabatically, though cooling arrangements may be provided where the temperature rise would be so high as to cause appreciable decomposition of the alkyl bromides formed. Such decomposition which becomes significant at the upper end of the temperature range leads to the production of olefins, which react in turn with bromine to form di-bromo alkanes; excessive temperatures should in consequence be avoided due to the larger amounts of by-products formed. The gaseous product withdrawn from the bromination reactor consists mainly of alkane, alkyl bromide and hydrogen bromide and is treated as described below.

When the bromine is introduced into the bromination reactor in solution, two effluent streams are withdrawn from the reactor, a liquid effluent consisting of aqueous hydrogen bromide poor in bromine, and a gaseous effluent consisting largely of alkane and alkyl bromide which may contain smaller amounts of hydrogen bromide. The bulk of the hydrogen bromide formed during the reaction dissolves in the aqueous solution.

Whether bromine in the form of vapour or in aqueous solution is used in the bromination reaction the gaseous effluent may be freed of hydrogen bromide by cooling and scrubbing with water or dilute aqueous hydrogen bromide to dissolve the hydrogen bromide present in the effluent. Where there are traces of bromine present in the effluent, it may be scrubbed first with aqueous hydrogen bromide to remove the bromine, but this is not normally necessary. The scrubbing may be carried out in scrubbers separate from the bromination reactor, or, when there are only small amounts of hydrogen bromide present in the gaseous product in the upper part of the bromination reactor. In the latter case scrubbing liquid may be allowed to run down into the reactor proper to act as a temperature regulator.

The residual gaseous effluent after removal of hydrogen bromide may then be cooled, suitably to a temperature in the range of 0° to 50°C. to condense all or part of the alkane, alkyl bromide, polybromoalkanes and residual water present in the gas. For C₃ to C₄ alkanes substantially all the alkane and alkyl bromide is condensed by cooling to 50°C., but for the lightest alkanes, particularly methane and ethane, condensation is incomplete. The condensate may be separated into two liquid phases, an organic phase consisting of al-

kane, alkyl bromide and polybromoalkanes, and an aqueous phase. The liquid organic phase is fractionated to separate it into an alkane fraction, an alkyl bromide fraction and a polybromoalkanes fraction. The alkane fraction and any uncondensed alkane after removal of impurities and preheating as necessary, are recycled to the bromination step.

Alternatively, particularly for C_1 to C_4 alkanes, the alkyl bromide may be separated from the gaseous effluent remaining after removal of hydrogen bromide, by scrubbing it with a suitable scrubbing liquid. It is convenient to use as the scrubbing liquid the corresponding polybromo-alkanes formed as by-products during the reaction. On scrubbing the residual gaseous effluent with these compounds, the alkyl bromide and polybromo-alkanes present in the effluent are preferentially dissolved. The undissolved alkane, after removal of impurities and preheating as necessary, is recycled to the bromination reaction zone. The solution of alkyl bromide in polybromo-alkanes is fractionated to separate the alkyl bromide and the polybromo-alkanes are recycled for use as scrubbing liquor.

Any excess polybromo-alkanes not required for the process may be removed from the system and disposed of as such or sent to a bromine recovery system, from which the recovered bromine may be returned to the process, preferably as an aqueous hydrogen bromide solution.

The alkyl bromide recovered from the bromination reaction products may, according to the invention, be converted to the corresponding alkanol by hydrolysis. Water or steam may be used as the hydrolysing agent. The hydrolysis may be carried out in the vapour phase using steam at high pressure, but, to avoid the need for vaporisation of large quantities of water, is preferably carried out in the liquid phase using water.

Liquid phase aqueous hydrolysis may be carried out at a temperature in the range of 80° to 200°C ., preferably 100° to 150°C ., and a pressure sufficient to maintain a liquid phase in the reaction zone. The amount of water added to the hydrolysis reaction should be sufficient to avoid high concentrations of hydrogen bromide being built up. Preferably the ratio by weight of water to hydrogen bromide exceeds 4 to 1 in the effluent from the hydrolyser. Higher concentrations of hydrogen bromide slow down the rate of reaction and increase the corrosiveness of the hydrolysate.

Preferably some of the product alkanol removed in the effluent from the hydrolysis reaction is recycled to that reaction together with any unreacted alkyl bromide. The recycle of alkanol has the advantage of increasing the solubility of bromide in the aqueous alcohol phase, thereby allowing the reaction to proceed more rapidly. The unreacted alkyl

bromide and sufficient alkanol for recycle may be separated from the effluent from the hydrolysis reaction by a suitably controlled fractionation step.

Small quantities of the corresponding dialkyl ether are formed during the hydrolysis and these may be recovered as such from the withdrawn effluent, e.g. by fractionation, or recycled to the hydrolysis reaction where they may be converted to the alkanol.

The residual liquid effluent is fractionated to recover alkanol which may contain water as the only significant impurity.

Hydrogen bromide is recovered from both the bromination and the hydrolysis reactions. That recovered from the bromination step is oxidised to produce bromine and, when hydrogen bromide is available from the hydrolysis step, it is oxidised together with the former.

The oxidation may be carried out either in the liquid phase or in the vapour phase, but is preferably carried out in the liquid phase to avoid the need for vaporisation of the hydrogen bromide solution in which form the hydrogen bromide is normally obtained.

Liquid phase oxidation of the hydrogen bromide may be controlled so that substantially all the bromine produced dissolves in the aqueous phase and does not form a separate phase. The reaction is desirably carried out at a temperature from 15° to 200°C ., preferably 50° to 130°C . and a pressure sufficient to maintain a liquid phase in the reaction zone.

The oxidation may suitably be carried out using either molecular oxygen or nitric acid. Molecular oxygen may be used alone or diluted with inert gases, e.g. in the form of air. A catalyst such as nitric oxide or nitric acid, or a nitrate or nitrite or other nitrogen containing compound capable of liberating nitric oxide or nitrogen dioxide is preferably also present.

When nitric acid is employed as the oxidising agent for the reaction, the nitric acid is largely converted to nitric oxide and nitrosyl bromide in the course of the reaction. The nitrosyl bromide thus formed may be decomposed by contacting it with water or aqueous hydrogen bromide to produce further nitric oxide. All or part of the nitric oxide may then be oxidised to nitric acid by contact with air and water as is well known in the art, and the nitric acid thus produced recycled to the oxidation reaction.

Any organic impurities present in the solutions fed to the oxidation reaction zone are largely oxidised to carbon dioxide and water. The carbon dioxide and the other waste gases may be vented, and the solution of bromine in aqueous hydrogen bromide collected and either passed directly to the bromination reaction or stripped of bromine and the bromine passed as vapour to the bromi-

nation reaction. In the latter case, the residual solution may be returned to the oxidation reaction or used as scrubbing liquor.

It will be appreciated that the invention provides a simple and convenient process for the conversion of a lower alkane to a corresponding alkanol employing only mildly exothermic reaction steps operating at moderate temperatures. The process is well-suited for continuous operation and, apart from alkane and oxygen, consumes only make-up quantities of bromine and catalysts.

Methods of procedure according to the invention are described below with reference to the accompanying drawings of which:

Figure 1 is a flow scheme of one method of carrying out the process of the invention, applied to the production of ethyl bromide or ethanol from ethane, and

Figure 2 is a flow scheme of another method of carrying out the invention applied to the production of *n*-amyl bromides of *n*-amyl alcohols from *n*-pentane.

Referring to Figure 1, fresh gaseous ethane feed is introduced under pressure into the system via line 1, recycle ethane leaving gas booster 100 is added via line 2, and the combined stream passes to the preheater 101 and thence via line 3 to the bromination reactor 102. Bromine vapour, together with some water vapour, is fed to the reactor 102 via line 4.

The hot gaseous product leaving the bromination reactor 102 via line 5 passes to the quench scrubber 103, where it is brought into contact with a dilute aqueous hydrogen bromide solution fed in via line 6. The gas-liquid mixture leaving scrubber 103 passes via line 7 to the gas-liquid separator 104. Liquid consisting of a more concentrated solution of hydrogen bromide in water leaves the separator 104 via line 8 and passes to the oxidizer 113 referred to later.

Gas consisting mainly of ethane, bromoethanes and water vapour and substantially free from hydrogen bromide passes from the separator 104 via line 9 to the cooler-condenser 105. Liquid and uncondensed gas pass from cooler 105 by line 10 to the separator 106 where the mixture is separated into a gas stream leaving by line 11, a condensing bromo-ethane stream leaving by line 12, both of which pass to the absorber 107, and condensed water which leaves by line 13. The absorber 107 has a lower stripping section of smaller diameter than the main part of the column and equipped in the base with a reboiler (not shown), the function of which is to strip dissolved ethane from the liquid which leaves the base of the column by line 14 and passes to the fractionating column 108 where ethyl bromide is separated as overhead product from dibromoethanes and higher brominated products, which leave the base of the column 108 via line 15.

The greater part of the separated dibromoethanes and higher brominated products are cooled and then recirculated as scrubbing liquid to the top of the absorber 107 via line 16 whilst a smaller amount which approximately balances the production of these compounds in the bromination reactor 102 leaves the system via line 17. These compounds may either be worked up in a separate unit into saleable products, or passed to a different unit in which bromine is recovered in a convenient form for return to the process, i.e., as an aqueous solution of hydrogen bromide by line 33.

Ethyl bromide recovered as the overhead product from column 108 passes to the base of the hydrolysis reactor 109 via lines 18 and 19. Process water is routed to the hydrolyser 109 via lines 13 and 27, 20 and 19 being suitably preheated before entering the hydrolyser and any excess or deficiency of water is removed from or supplied to the system via line 21.

The hydrolyser 109 consists of a vertical tower equipped with internal baffles and an agitator in the lowest zone to secure intimate mixing of the separate liquid phases. Undissolved ethyl bromide remains substantially in the bottom zone of the hydrolyser, but ethyl bromide in solution in the aqueous-alcoholic phase passes into the middle and upper zones of the hydrolyser where its concentration is progressively reduced by chemical reaction with the solvent.

The liquid product from the hydrolyser is passed via line 22 to the fractionating column 110 in which unreacted ethyl bromide together with any diethyl ether formed and some of the ethanol is removed as overheads product and returned to the hydrolyser via line 23. The bottoms product from column 110 passes via line 24 to the fractionating column 111 from which the ethanol product consisting of at least 90% ethanol is removed by line 25 as overhead product. The bottoms product from column 111 consisting of an aqueous solution of hydrogen bromide, passes by line 26 to a further fractionating column 112, from which some of the water contained in the feed is removed by line 27 as overhead product and recycled to the hydrolyser 109. The bottoms product from column 112 leaves by line 28 which joins aqueous hydrogen bromide from line 8 and passes via line 29 to the stirred liquid phase oxidizer 113. This is supplied with oxygen via line 30 and nitric acid catalyst via line 31. Bromine make-up and recovered bromine from the bromine recovery unit are supplied to the oxidizer as an aqueous solution of hydrogen bromide by line 33.

A solution of bromine in aqueous hydrobromic acid from the oxidizer 113 passes via line 34 to the upper part of the stripping column 114 from the top of which bromine is

removed as a vapour together with some water vapour and passes via line 4 to the bromination reactor 102. A hot dilute aqueous hydrogen bromide solution leaves the base of column 114 and is passed to scrubber 103 via line 6.

The above description with reference to Figure 1, refers to the production of ethanol from ethane but the process and apparatus described may also advantageously be used for the production of methanol from methane.

Referring to Figure 2 which represents a scheme particularly suitable for the production of secondary normal amyl alcohols from normal pentane, the fresh hydrocarbon feed enters the process as a liquid from storage via line 1, is mixed with liquid recycle hydrocarbon from line 2 and passes to the vapourizer-preheater 101 which is equipped for steam or any other convenient form of heating. The preheated hydrocarbon vapour passes via line 3 to the reactor 102. Bromine vapour, together with some water vapour, is fed via line 4 to the bromination reactor 102.

In the reactor 102 substantially all the bromine reacts with the alkane to form a gaseous mixture containing unreacted alkane alkylbromide, hydrogen bromide and polybromo-alkanes. The hot gaseous product leaving the bromination reactor 102 via line 5 passes to the quench scrubber 103 where it is brought into contact with dilute solution of hydrogen bromide fed in via line 6. The gas-liquid mixture leaving scrubber 103 passes via line 7 to the gas-liquid separator 104. Liquid consisting of a more concentrated solution of hydrogen bromide in water leaves the separator 104 via line 8 en route to the oxidizer 113 (referred to hereinafter).

A vapour mixture of pentane, bromopentanes and water and substantially free from hydrogen bromide passes from the separator 104 via line 9 to the condenser 105. Condensed liquid from condenser 105 passes via line 10 to the separator 106 where it separates into a pentane-bromopentane phase which passes via line 11 to the fractionating column 107 and an aqueous phase which leaves via line 13 en route to the hydrolyser 109. The mixture entering column 107 is separated into an overhead stream consisting of unreacted pentane which leaves en route to the bromination reaction via line 2 and a bottoms product consisting of bromopentanes which passes via line 14 to the further fractionating column 108; here it is separated into an overhead product consisting of monobromopentanes which leaves via lines 18, 19 to the hydrolyser 109 and a bottoms product consisting of dibromopentanes and higher boiling materials which leaves by line 17 and passes to a separate bromine recovery unit.

Water from the separator 106 passes to the hydrolyser 109 via lines 13, 20 and 19 and any surplus or deficiency of water in the

process is adjusted by bleeding water out of or into the process via line 21. A second aqueous phase containing some dissolved pentanols and obtained from a later stage of the process passes into the hydrolyser by lines 27 and 20 and 19. Part of the aqueous streams fed to the hydrolyser is suitably preheated. Alcohol containing any unreacted bromopentanes from the hydrolyser is recycled to the hydrolyser via lines 35 and 19 from storage or from a separate pentanol purification unit.

The hydrolyser 109 consists of a vertical pressurised tower equipped with internal baffles and an agitator in the lowest zone to secure intimate mixing of the separate liquid phases. Undissolved bromopentanes remain substantially in the lowest zone of the hydrolyser, but bromopentanes in solution in the aqueous pentanol phase pass into the middle and upper zones of the hydrolyser where their concentration is progressively reduced by chemical reaction with the solvent.

The liquid leaving the hydrolyser passes via line 22 to the fractionating column 110 which is equipped with an overhead condenser 115 and a phase separator or decanter 116. Overhead vapour leaving the column via line 23 and consisting of water, pentanol and unreacted bromopentanes is condensed and cooled in condenser 115, and the resulting condensate passes via line 24 to the separator 116 where the aqueous and sparingly soluble pentanol phases separate. The aqueous phase leaves via line 27, part being returned as reflux to the column 110 via line 26, the remainder being recycled to the hydrolyser 109. Crude pentanol product leaves the system via line 25 and may be used as such or further purified in another unit where it may be conveniently fractionated to give a bromopentane rich stream which is returned to the hydrolyser via line 35 and in which secondary normal pentanols are separated by distillation from primary normal pentanol which is formed in smaller quantities as a by-product.

The bottoms product from fractionator 110 consisting of a moderately concentrated solution of hydrogen bromide in water leaves via line 28 and after joining the aqueous hydrogen bromide leaving separator 104 via line 8, passes to the oxidizer 113 via line 29.

Oxygen is continuously supplied to the oxidizer via line 30, nitric acid catalyst via line 31 and recovered and make-up bromine via line 33 as a solution of hydrobromic acid in water. Inert gas is continuously vented from the oxidizer via line 32. The oxidizer is provided with a stirrer. The oxidized product consisting of a solution of bromine in hydrobromic acid is continuously returned to the stripper 114 via line 34.

In the stripper 114 a gaseous overhead product comprising bromine with a little water vapour is removed and passed via line 4 to reactor 102. The residual liquid consisting of

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hot dilute aqueous hydrogen bromide leaves the base of the stripper 114 via line 6 and is passed to the scrubber 103.

The system illustrated by Figure 2 may suitably be applied to the production of cycloalkyl bromides and cycloalkanols from the corresponding cycloalkanes having 5 to 8 carbon atoms, e.g. the production of cyclohexyl bromide and cyclohexanol from cyclohexane. An advantage of the process of the invention as compared with the oxidation process for the production of cyclohexanol is the absence of cyclohexanone from the product of the reaction. The invention is also applicable to alkyl-substituted cycloalkanes.

The fractionating columns shown in Figures 1 and 2 are provided as required with reboilers, reflux condensers, pumps, vessels and other auxiliaries. The processes are fully continuous. Special corrosion resistant materials, for example titanium and its alloys, are employed as required by the corrosive nature of the process fluids.

The following Examples 1 and 2 illustrate the bromination and hydrolysis steps of the process of the invention. When combined with hydrogen bromide oxidation such as illustrated in Examples 3 and 4 they illustrate the whole process of the invention. In the Examples parts and percent means parts by weight and percent by weight respectively unless otherwise indicated.

EXAMPLE 1

Ethane and bromine in a molar ratio of 9:1 were reacted in the vapour phase in an elongated reactor. The reaction temperature was 303°C., the reaction pressure 1 atmosphere absolute and the contact time in the hot reaction zone 14 secs. The reactor product was analysed and found to be free of bromine. Of the organic brominated product 87.4% was ethyl bromide and 12.6% dibromoethanes and higher brominated products. Thus, about 84% of the theoretical yield of ethyl bromide, based on bromine utilized, was obtained.

In another run ethane and bromine in a molar ratio of 3.2 to 1 were reacted in the vapour phase in a similar reactor. The reaction temperature was 319°C., the reaction pressure 1 atmosphere absolute and the contact time 39 secs. Again the reactor product contained no free bromine. 77.4% of the organic brominated product was ethyl bromide and 22.6% dibromo-ethanes and higher brominated products. Comparison of the two runs clearly indicates the importance of excess alkane in reducing the amount of polybromo-compounds produced.

1 part of ethyl bromide produced as described above was added to 9 parts of an ethanol-water mixture consisting of 40% ethanol and 60% water, and hydrolysed for 2 hours at 130°C. and 20 atmospheres pres-

sure. 93% of the ethyl bromide present was hydrolysed and the yield of ethyl alcohol, based on ethyl bromide hydrolysed, was over 97%.

EXAMPLE 2

A mixture of *n*-pentane (92% pure), and bromine vapour in a molar ratio of 4.7 to 1 was reacted in an elongated reactor the first part of which was maintained at a temperature of 265°C. The reaction pressure was one atmosphere absolute and the contact time in the hot reaction zone 12 secs. The effluent gases were passed through a scrubber maintained at 70°C. through which water was circulated, and then to a condenser in which the vapours were completely condensed. The bromine was quantitatively converted to hydrogen bromide and organic bromine compounds. 47% of the bromine introduced was found as hydrogen bromide dissolved in the scrubbing water.

The condensed phase was fractionated and analysed. 86% of the organic bromine compounds were found to monobromopentanes and 14% higher brominated products. The monobromopentanes were made up as follows:

1-bromo- <i>n</i> -pentane	13%
2-bromo- <i>n</i> -pentane	47%
3-bromo- <i>n</i> -pentane	31%
unidentified	9%

One part of the mono-bromo-pentanes obtained as above was hydrolysed with 15 parts of a 15% alcohol-85% water mixture for three hours at 145°C. 91% of the monobromo-pentanes was hydrolysed, with a yield of 92% of alcohols based on the bromopentanes hydrolysed.

The oxidation of hydrogen bromide using nitric acid as the oxidising agent recovered from the bromination and hydrolysis steps is illustrated in the following two Examples.

EXAMPLE 3

100 parts of an aqueous solution containing 20 parts of hydrogen bromide representing a typical product from the base of column 112 and separator 104 of Fig. 1 was refluxed for one hour with 5 parts of nitric acid. Evolution of nitric oxide gas which was rapid during the first 15 minutes became thereafter progressively slower and was negligible at the end of the period.

The liquid reaction product was distilled for 1½ hours to remove dissolved nitrosyl bromide, water lost by distillation being replenished every half hour. Bromine and water were collected in the distillate.

Analysis of the residue indicated that 89% of the original nitric acid and 82% of the original hydrogen bromide had reacted. The conversions corresponded closely to the reaction of one mole of nitric acid with three moles of hydrogen bromide.

EXAMPLE 4

The experiment described above was repeated employing 100 parts of an aqueous solution containing 20 parts hydrogen bromide and 3 parts of nitric acid. The final analyses indicated that 94% of the original nitric acid and 53% of the original hydrogen bromide had reacted, again corresponding closely to the reaction of 1 mole of nitric acid with three moles of hydrogen bromide.

The bromine produced in each of Examples 3 and 4 was suitable for recycle for use in the bromination of additional quantities of alkane.

The bromination reactor 102 in Figures 1 and 2 may suitably consist of two consecutive reaction zones — an initial zone of diameter equal to at least half its length and designed to promote a high degree of mixing throughout the zone, and a final zone of smaller diameter but greater length than the initial zone in which back-mixing is minimised. The greater part of the reaction and consequent liberation of heat then takes place in the initial zone, thereby quickly preheating the incoming streams of bromine and alkane to a temperature at which the rate of reaction is rapid. The initial zone may be provided with a means for local heating, e.g. a suitably sheathed electric element, to initiate the reaction at plant start-up. The final zone is intended to achieve substantially complete conversion of bromine whilst avoiding the formation of excessive amounts of polybromoalkanes.

If required, an additional scrubber or other device, designed to eliminate mist caused by fine droplets of aqueous hydrogen bromide, may be provided in line 7 of Figure 1 or line 9 of Figure 2 to treat the gas leaving the first scrubber.

The process of this invention using an alkane and bromine as starting materials has two important advantages when compared with a process using chlorine in place of the bromine. Firstly, the alkyl bromides formed are more readily hydrolysed to the alcohol than are the corresponding alkyl chlorides, and satisfactory rates of hydrolysis of the bromides may be achieved in liquid phase hydrolysis at only moderately elevated pressures and at temperatures below 150°C. Secondly, hydrogen bromide is more readily and economically oxidised to bromine than hydrogen chloride is oxidised to chlorine, and hydrogen bromide may be oxidised easily in aqueous solution.

WHAT I CLAIM IS:—

1. A process for the production of a lower alkanol from the corresponding alkane, which comprises reacting an excess of the alkane with bromine at an elevated temperature to produce the corresponding alkyl bromide and hydrogen bromide, separating the alkyl bromide and subjecting it to hydrolysis at an

elevated temperature with water or steam as the hydrolysing agent to produce the corresponding alkanol and hydrogen bromide, recovering the alkanol, oxidising hydrogen bromide recovered from the products of the bromination step and from the products of the hydrolysis step to produce bromine and recycling the bromine thus produced to the bromination step.

2. A process for the production of a lower alkyl bromide from a corresponding alkane which comprises reacting an excess of the alkane with bromine at an elevated temperature to produce the alkyl bromide and hydrogen bromide, separating the hydrogen bromide from the alkyl bromide, recovering the alkyl bromide, oxidising hydrogen bromide separated to produce bromine and recycling the bromine to the bromination step.

3. A process as claimed in Claim 1 or 2, wherein the bromination reaction is carried out at a temperature of from 80° to 450°C. and a pressure of from 1 to 200 atmospheres absolute.

4. A process as claimed in Claim 3 wherein the bromination reaction is carried out with bromine in the vapour phase in the absence of a catalyst at a temperature from 200° to 350°C. and a pressure from 1 to 15 atmospheres absolute.

5. A process as claimed in Claim 3 wherein the bromination reaction is carried out using bromine in solution in aqueous hydrogen bromide in the presence of a free radical-generating catalyst or initiator at a temperature from 125° to 180°C. and a pressure sufficient to prevent appreciable evaporation of the aqueous hydrogen bromide.

6. A process as claimed in any of the preceding claims wherein the molar ratio of alkane to bromine in the bromination step is from 3 to 1 to 10 to 1.

7. A process as claimed in Claim 4 or Claim 4 and 6 wherein a gaseous stream containing unreacted alkane, alkyl bromide, polybromoalkanes and hydrogen bromide is withdrawn from the bromination step, is scrubbed with water or dilute aqueous hydrogen bromide to absorb the hydrogen bromide, and, after removal of water, alkyl bromide is separated from the residual gaseous effluent.

8. A process as claimed in Claim 7 wherein the residual gaseous effluent, after removal of water, is cooled and fractionated to separate an alkane fraction which is recycled to the bromination step, an alkyl bromide fraction and a polybromoalkanes fraction.

9. A process as claimed in Claim 7 wherein the residual gaseous effluent is scrubbed with liquid polybromoalkanes to absorb alkyl bromide and polybromoalkanes, the unabsorbed alkane is recycled to the bromination step, the scrubber liquid is fractionated to separate alkyl bromide from polybromoalkanes and the

- polybromoalkanes are recycled to the scrubbing step.
10. A process as claimed in Claim 1 or in Claim 1 and any of Claims 3 to 9, wherein the hydrolysis of the alkyl bromide is carried out in the liquid phase at an elevated temperature using water as the hydrolysing agent, a liquid effluent comprising water, hydrogen bromide and alkanol is removed from the reaction zone, and the alkanol is recovered from this liquid effluent.
11. A process as claimed in Claim 10 wherein the hydrolysis is carried out at a temperature from 100° to 150°C. at a pressure sufficient to prevent appreciable evaporation of the liquid phase.
12. A process as claimed in Claim 10 or 11, wherein a part of the product alkanol removed from the hydrolysis zone is recycled to that zone to dissolve alkyl bromide.
13. A process as claimed in any of Claims 10 to 12, wherein the ratio by weight of water to hydrogen bromide in the hydrolysis zone is maintained above 4 to 1.
14. A process as claimed in any of Claims 10 to 13, wherein the liquid effluent removed from the hydrolysis zone is fractionated to separate an alkanol product fraction containing water as substantially the only impurity, an unreacted alkyl bromide fraction and an aqueous hydrogen bromide fraction.
15. A process as claimed in any of the preceding claims, wherein the hydrogen bromide oxidation is carried out in aqueous solution at an elevated temperature to form a solution of bromine in aqueous hydrogen bromide.
16. A process as claimed in Claim 15, wherein the oxidation is carried out at a temperature from 50° to 130°C. and a pressure sufficient to prevent appreciable evaporation of the aqueous solution.
17. A process as claimed in any of the preceding claims, wherein the hydrogen bromide is oxidised with molecular oxygen or nitric acid.
18. A process as claimed in Claim 17, wherein molecular oxygen is the oxidising agent and nitric oxide, nitric acid, or a nitrate or nitrite capable of yielding nitric oxide or nitrogen dioxide, is added as a catalyst.
19. A process as claimed in Claim 17, wherein nitric acid is the oxidising agent and nitric oxide formed during the oxidation and/or by decomposition of nitrosyl bromide formed during the oxidation, is oxidised to nitric acid which is recycled to the hydrogen bromide oxidation step.
20. A process as claimed in any of the preceding claims, wherein the starting alkane is methane and methyl bromide or methanol, as the case may be, is produced as product.
21. A process as claimed in any of Claims 1 to 19 wherein the starting alkane is ethane and ethyl bromide or ethanol, as the case may be, is produced as product.
22. A process as claimed in any of Claims 1 to 19, wherein the starting alkane is a normal paraffin with 3, 4 or 5 carbon atoms and the corresponding alkyl bromide or secondary normal alcohol, as the case may be, is produced as product.
23. A process as claimed in any of Claims 1 to 19, wherein the starting alkane is a cycloalkane or alkyl-substituted cycloalkane having at least 5 carbon atoms in the cycloalkane ring and the corresponding cycloalkyl bromide or cycloalkanol, as the case may be, is produced as product.
24. A process for the production of a lower alkyl bromide as claimed in claim 2 substantially as herein described.
25. A lower alkyl bromide when produced by a process claimed in Claim 2 or in Claim 2 and any of Claims 3 to 9 and 15 to 23 or in Claim 24.
26. A process for the production of a lower alkanol as claimed in claim 1 substantially as hereinbefore described.
27. A lower alkanol when produced by the process claimed in Claim 1 or in Claim 1 and any of Claims 3 to 23 or in Claim 26.

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