(54) Title: FUEL SYNTHESIS

(57) Abstract: A method of transforming a normally gaseous composition containing carbon dioxide and at least one normally gaseous hydrocarbon into a product stream containing at least one normally liquid hydrocarbon; the method comprising the steps of feeding the composition into a reactor including a first electrode means, a second electrode means and at least one layer of a normally solid dielectric material positioned between the first and the second electrode means; submitting the composition within the reactor in the presence of a normally solid catalyst to a dielectric barrier discharge, wherein the normally solid catalyst is a member selected from the group of zeolites, modified zeolites and zeolite-like materials, and wherein the normally solid catalyst has an at least partially crystalline solid structure with at least one 10-ring channel or with at least one 12-ring channel; and controlling the dielectric barrier discharge to convert the normally gaseous composition into the product stream.

FUEL SYNTHESIS

5   Background of the Invention

       The present invention relates to a method of
       transforming a normally gaseous composition containing
       carbon dioxide and at least one normally gaseous
10   hydrocarbon into a product stream containing at least one
       normally liquid hydrocarbon, furthermore the present
       invention relates to a normally liquid fuel and to an
       apparatus for transforming a normally gaseous composition
       containing carbon dioxide and at least one normally gaseous
15   hydrocarbon into a product stream containing at least one
       normally liquid hydrocarbon.

       One of the major problems facing mankind is the global
       warming of the atmosphere due to man-made emissions of
20   greenhouse gases such as carbon dioxide, methane, chloro-
       fluorocarbons, nitrous oxide or ozone. One possible appro-
       ach to mitigate the emissions of these greenhouse gases to
       the atmosphere would be to recycle them in a chemical
       process to form useful products. Among all the man-made
25   greenhouse gases, methane and carbon dioxide contribute to
       most of the greenhouse effect.

       Prior Art
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       There are two general pathways to upgrade methane being
       the principal constituent of natural gas into higher

hydrocarbons. First, by way of indirect conversion mainly requiring syngas production in a first step, and second, by way of direct conversion. A major difficulty, in particular for direct methane conversion, is the high strength of the

5   C-H bonds in the methane molecule causing methane to be a very stable molecule and its reactions to have a high activation energy. There are many ways to activate methane such as photochemical and electrochemical activation, laser-induced activation, and radiolysis, as well as

10   catalytic or even thermal activation. The direct methane conversion methods include, e.g. oxidative coupling, partial oxidation to methanol and formaldehyde, non-oxidative routes and organometallic routes. However, the direct methane transformations into higher hydrocarbons

15   show, so far, poor economics, low conversions and low yields making them not suitable for practical applications.

A great effort has also been given to chemical fixation of carbon dioxide. Heterogeneous catalysis has been

20   considered to be a desirable route for carbon dioxide utilization. But a large amount of additional energy or expensive hydrogen is required for conventional catalytic utilization of carbon dioxide since the carbon dioxide molecule has a very low energy content. There is still no

25   confirmed technology by far for utilizing such a plentiful carbon source.

A few processes for the synthesis of liquid fuel, such as normally liquid hydrocarbons, starting from gaseous

30   compositions are known, such as the "Mobil process" and the "Fischer-Tropsch process" schematically shown in equation (1) and (2).

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$$CO + H_2 \quad\quad \rightarrow \quad CH_3OH \rightarrow \quad gasoline \quad\quad\quad (1)$$

$$CO + H_2 \quad\quad \rightarrow \quad\quad gasoline \quad\quad\quad (2)$$
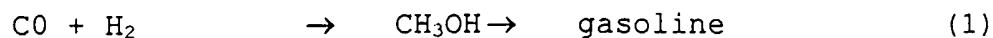
For both heterogeneous catalyzed processes the production of "synthesis gas", a mixture of CO and H_2 also named "syngas", represents the first step along the path to methanol and gasoline respectively. Even if the "Mobil process" (eq. (1)) and the "Fischer-Tropsch process" (eq. (2)) are practiced today for industrial fuel synthesis production, e.g. in South Africa, Malaysia and New Zealand, they are non-economic "political processes", heavily supported by governmental subsidies. The lack of profitableness is either due to the usually required high pressures at which the processes take place as well as to the high production costs of syngas and the fact that the produced syngas needs to be compressed before applied in the processes (1) and (2). Thus, about 60% to 80% of the total cost of the processes (1) and (2) goes to production and compression of syngas.

The industrial production of syngas mostly derives from the energy-intensive steam reforming of methane shown in equation (3):

$$H_2O + CH_4 \quad \rightarrow \quad CO + 3\ H_2 \quad\quad \Delta H° = 206.1\ kJ/mol \quad (3)$$

Syngas can also be produced from the greenhouse gases methane and carbon dioxide as shown in equation (4). However, such a reforming of carbon dioxide by methane is also a very energy-intensive process and requires high tempera-

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tures. Moreover, deposition of carbon on the catalyst always causes problems for this reaction.

$$CO_2 + CH_4 \quad \rightarrow \quad 2\ CO + 2\ H_2 \qquad \Delta H^\circ = 258.9\ kJ/mol$$

5   (4)
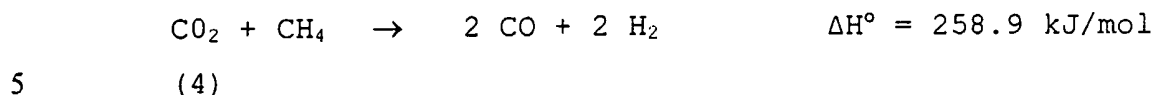
Non-equilibrium plasma chemical processes occurring in the volume part of electrical non-equilibrium discharges have attracted a great deal of interest. Particularly,

10   silent gas discharges have demonstrated their suitability for large-scale industrial applications, such as the generation of ozone. A characteristic of the silent discharge is the presence of a dielectric. Therefore silent gas discharges are also referred to as dielectric barrier

15   discharges.

Recently, the utilization of greenhouse gases for the synthesis of methanol or methane in such silent gas discharge reactors has also been described. Thus, DE 42 20 865

20   describes a method and an apparatus for the hydrogenation of carbon dioxide leading in particular to methane or methanol by exposing a mixture of carbon dioxide and a substance containing hydrogen atoms, preferably hydrogen or water, to a dielectric barrier discharge. An overview of

25   the progress in this field have been summarized by Bill et al. in Energy Conversion Management 38 (1997) 415 (this report being incorporated herein for all purposes by way of reference). It is noteworthy, however, that the reported maximum yield of methanol was only about 1%.

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Objects of the Invention

Accordingly, it is an object of the present invention
to provide for a method of transforming a normally gaseous
5   composition into a product stream containing at least one
normally liquid hydrocarbon, which method minimizes or even
avoids the disadvantages of the prior art.

Moreover, it is an object of the present invention to
10   provide for a method of transforming a normally gaseous
composition into a product stream containing at least one
normally liquid hydrocarbon, which method can be carried
out at low pressures, and preferably at low temperatures.

15   It is another object of the present invention to provi-
de for a method of producing liquid fuel and gasoline,
respectively, from carbon dioxide and at least one normally
gaseous hydrocarbon in reasonable yields and in a direct
manner, i.e. making the expensive formation of syngas no
20   longer necessary.

It is a further object of the present invention to
provide for a method of producing liquid fuel and gasoline,
respectively, from carbon dioxide and at least one normally
25   gaseous hydrocarbon in reasonable yields and in a direct
manner, which gasoline is rich in C6 to C10 hydrocarbons.

Another object of the present invention is to provide
for an apparatus that allows the transformation of a gase-
30   ous composition containing carbon dioxide and at least one
normally gaseous hydrocarbon into a product stream
containing at least one normally liquid hydrocarbon.

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Further objects and advantages of the present invention will become apparent as this specification proceeds.

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Brief Summary of the Invention

We have found that the objects can be achieved according to a first general embodiment of the invention by a
10   method as set forth in claim 1. Accordingly, the invention provides for a method of transforming a normally gaseous composition containing carbon dioxide and at least one normally gaseous hydrocarbon into a product stream containing at least one normally liquid hydrocarbon; said
15   method comprising the steps of feeding said composition into a reactor including a first electrode means, a second electrode means and at least one layer of a normally solid dielectric material positioned between said first and said second electrode means; submitting said composition within
20   said reactor in the presence of a normally solid catalyst to a dielectric barrier discharge, wherein said normally solid catalyst is a member selected from the group of zeolites, modified zeolites and zeolite-like materials, and wherein said normally solid catalyst has an at least
25   partially crystalline solid structure with at least one 10-ring channel; and controlling said dielectric barrier discharge to convert said normally gaseous composition into said product stream.

30   In a second general embodiment the invention provides for a method of transforming a normally gaseous composition containing carbon dioxide and at least one normally gaseous

hydrocarbon into a product stream containing at least one
normally liquid hydrocarbon; said method comprising the
steps of feeding said composition into a reactor including
a first electrode means, a second electrode means and at

5   least one layer of a normally solid dielectric material
positioned between said first and said second electrode
means; submitting said composition within said reactor in
the presence of a normally solid catalyst to a dielectric
barrier discharge, wherein said normally solid catalyst is

10   a member selected from the group of zeolites, modified
zeolites and zeolite-like materials, and wherein said
normally solid catalyst has an at least partially
crystalline solid structure with at least one 12-ring
channel; and controlling said dielectric barrier discharge

15   to convert said normally gaseous composition into said
product stream.

       In a third general embodiment the invention provides
for a normally liquid fuel obtainable by a dielectric bar-

20   rier discharge, the normally liquid fuel comprising at
least 60 mol% of hydrocarbons having a normal boiling range
of between about 50°C and about 210°C, and less than 40 mol%
of oxygenated hydrocarbons.

25   In a fourth and a fifth general embodiment the
invention provides for an apparatus for transforming a
normally gaseous composition containing carbon dioxide and
at least one normally gaseous hydrocarbon into a product
stream containing at least one normally liquid hydrocarbon

30   as set forth in claim 20 and in claim 28.

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Definitions, Detailed Description of Preferred Embodiments and Elements of the Invention

The term "about" as used herein before any numeral implies a variation of typically ± 10%.

The term "normal" with regard to boiling points, boiling ranges and the like indicates that these values are understood as being corrected for "normal conditions", i.e. a temperature of 25°C and an atmospheric pressure of 1013 mbar. In analogy, the term "normal" with respect to physical states of matter and the like indicates that they are referred to said "normal conditions".

The term "layer" is used herein to refer to any planar or curved stratum having a width dimension that is substantially larger than its thickness dimension; typically, the width:thickness ratio is at least 10:1 and generally well above that value.

In the context of the present invention the term "hydrocarbons" stands for substances consisting of hydrogen and carbon atoms, such as aliphatic hydrocarbons being either saturated, such as alkanes, or unsaturated, such as alkenes and alkynes, and cycloaliphatic being either saturated or unsaturated, and aromatic hydrocarbons. Hydrocarbons obtained by the inventive method generally do not contain pollutants, like sulfur and/or heavy metal elements. This represents a major advantage compared to hydrocarbons produced from petroleum, in particular, when the hydrocarbons are then used as fuel. Since the reservoir of natural gas is much larger compared to the one of petroleum

the present invention is therefore very valuable not only from an economic point of view but also taking ecological aspects into consideration.

5   Sources of gaseous compositions containing carbon dioxide and/or at least one normally gaseous hydrocarbon are for example fermentation gas, coal-bed gas, associated gas from crude oil or natural gas or any waste and exhaust gases deriving from industrial processes and containing
10   carbon dioxide and/or at least one normally gaseous hydrocarbon such as methane, ethane, n-propane or iso-propane. It is, however, in accordance with and within the scope of the present invention to use commercially available methane, ethane, n-propane or iso-propane and carbon
15   dioxide of any purity or any other source of these compounds known to the man skilled in the art.

       According to preferred embodiments of the present invention the at least one normally gaseous hydrocarbon is
20   selected from the group of methane, ethane and propane. It is obvious that a mixture of the aforementioned normally gaseous hydrocarbons and further normally gaseous hydrocarbons can be used for the present invention, as indicated above. Preferably the normally gaseous
25   composition contains methane.

       In further preferred embodiments of the present invention the carbon dioxide and the methane are contained in the normally gaseous composition at a molar ratio of
30   carbon dioxide:methane of between about 1:1 to about 1:4, preferably between about 1:2 to about 1:3.

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The normally solid catalyst is a "shape-selective catalyst" being selected from the group of zeolites, modified zeolites and zeolite-like materials and thus having an at least partially crystalline, typically

5   completely crystalline, solid structure. The term "shape-selective catalyst" is intended to refer to a catalyst that owns a special structure containing channels and pores, respectively, to limit the diffusion of the reacting molecules and the formed product molecules through its

10   framework. Only molecules with diameters smaller than the openings and apertures, respectively, of the channels can pass through the shape-selective catalyst. Moreover, an additional constraint is imposed by the size and shape of the apertures and channels with respect to possible transition

15   states of the reaction.

Zeolites are crystalline aluminosilicates of group IA and group IIA elements such as sodium, potassium, magnesium and calcium with the empirical formula (I)

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$$M_{2/n}O \cdot (1-y)Al_2O_3 \cdot ySiO_2 \cdot wH_2O \qquad\qquad (I)$$
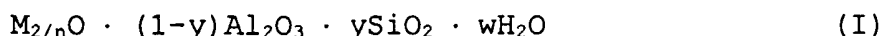
wherein   n is the valence of the cation M,
           y the molar fraction of SiO_2 in the zeolite
25   framework, and
           w number of water molecules present in the
           zeolite.

Zeolite structures are based on a three-dimensional
30   framework of AlO_4 and SiO_4 tetrahedra (Si and Al defined as T atoms) which are interlinked through common oxygen atoms forming O-T-O-T-O bonds to give said three dimensional

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network through which channels run. Each AlO_4 tetrahedron in
the framework bears a net negative charge which is
compensated by a cation of the aforementioned group IA and
group IIA elements. This cation is mobile and can be
5   exchanged by other cations. In the interior of the channels
are water molecules and the mentioned mobile cations.
Criteria to distinguish zeolites and zeolites structures,
respectively, are, inter alia, the number of either T- or
O-atoms forming the rings and openings, respectively,
10   controlling diffusion through the channels as well as the
molar ratio of SiO_2/Al_2O_3, in short the Si/Al ratio.

"Modified zeolites" as used herein refers to natural or
synthetic zeolites which have been modified by either
15   cation or ion exchange, thermal treatment, hydrothermal
treatment, treatment with inorganic or organic acids,
treatment with inorganic or organic F materials, i.e
inorganic or organic compounds containing fluor or
fluoride, as well as with organic silica materials, and, in
20   particular, by an isomorphic substitution of the T atoms.
Such an isomorphic substitution of the T atoms, e.g.
leading to silicoaluminophosphates, can be effected
particularly by changing the parameters of the zeolite
syntheses or by "post synthesis" modifications. Thus,
25   various T atoms can be introduced into a zeolite framework
during the synthesis step, such as Ga, Ge, Li, Be, B, Mg,
Ti, Mn, Fe, Co, In, As and H. Such an introduction of a
certain element and its concentration in a zeolitic
framework usually occurs by mixing the different components
30   in the synthesis gel. However, any other procedure for the
introduction of the mentioned and other elements leading to
modified zeolites are within the scope of the present

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invention. Moreover, the preparation method by simply
mixing the different components as well as other procedures
for the synthesis of modified zeolites are known by the
person skilled in the art and need no further explanation

5   herein. In analogy, "post synthesis" modifications of
zeolites, i.e. modifications of existing natural or
synthetic zeolites to effect a T-site substitution are also
within the knowledge of the artisan and do not need to be
further explained herein. Thus, various gaseous and liquid

10   reactants as well as different techniques, such as
hydrothermal techniques, have been developed for such a
post synthesis T-site substitution. In particular, numerous
reactants and techniques have been described for aluminium
removal with simultaneous substitution by other elements

15   such as Si, Ti, V, Fe, Sn, Ge and P.

"Zeolite-like materials" as used herein refers to
normally solid materials, such as aluminophosphates,
silicoaluminophosphates, metalloaluminophosphates and metal

20   oxides containing OH groups, which have solid structures
similar to zeolites and, therefore, which contain channels
with sizes and shapes similar to channel sizes and shapes
in zeolite structures. In particular, "zeolite-like
materials" refer to crystalline solids which have zeolite-

25   like structures as indicated by their incorporation in the
"Atlas of Zeolite Structure Types" reported by Meier and
Olson in "Atlas of Zeolites Structure Types", Zeolites
17(1996), 1-230 (report being incorporated herein for all
purposes by way of reference). Examples of those isotypic

30   and homeotypic species having zeolite-like structures are
reported, in particular, in Table 3 on page 14 of the
aforementioned reference.

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In accordance with the present invention it has been found that the use of a member selected from zeolites, modified zeolites and zeolite-like materials having at least one 10-ring channel or at least one 12-ring channel within its structure as the normally solid catalyst for the inventive method limits the growth of the hydrocarbon chain and thus inhibits the undesired formation of solid polymer. Consequently, an increased production and high yield, respectively, of liquid fuel, in particular of normally liquid hydrocarbons, results. Moreover, the application of shape-selective catalysts for the inventive method leads to a large amount of branched hydrocarbons, in particular branched normally liquid hydrocarbons, representing a higher-quality fuel.

Typical and preferred materials having a solid structure in accordance with the present invention, and having at least one 10-membered ring channel system within the structure, are given in the following by way of their structure type codes consisting of three capital letters. These structure type codes have been set up by the IUPAC Commission on Zeolite Nomenclature and are, inter alia, listed together with their basic structural features and specific examples of zeolites, modified zeolites and zeolite-like materials in the above-mentioned "Atlas of Zeolite Structure Types" reported by Meier and Olson in Zeolites 17(1996), 1-230. Thus, typical normally solid catalysts in accordance with the present invention having at least one 10-ring channel are of the structure type AEL, AFO, AHT, FER, LAU, MEL, MFI, MFS, MTT and STI. Typical and preferred materials having a solid structure in accordance

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with the present invention, and having at least one 12-
membered ring channel system within the structure, are of
the structure type AFI, AFR, BEA, LTL, MEI, MOR, ZSM-12 and
ZSM-18.

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In a further preferred embodiment of the present
invention, the at least one 10-ring channel has a diameter
of between about 4 Å and about 7 Å, whereas the at least
one 12-ring channel has preferably a diameter of between
10   about 4 Å and about 8 Å. Such well-defined pore systems
further increase the shape-selectivity of the normally
solid catalyst since the pores and channels, respectively,
must be capable to accommodate the reactants, i.e. the
normally gaseous composition, and in particular carbon
15   dioxide and the normally gaseous hydrocarbons or fragments
thereof. Moreover, an additional constraint is imposed by
the pores and apertures of the channels which control the
size and shape of the product molecules. Therefore, the
preferred diameter of the at least one 10-ring channel
20   between about 4 Å and about 7 Å and the preferred diameter
of the at least one 12-ring channel between about 4 Å and
about 8 Å, respectively, leads to a precisely defined
arrangement of AlO_4 and SiO_4 tetrahedra and thus to a shape-
selective dielectric barrier discharge reaction with good
25   reproducibility.

In further preferred embodiments of the present
invention the solid structure of the normally solid
catalyst have at least two channel systems, wherein at
30   least one channel system is either a 10-ring channel or a
12-ring channel. Typically these at least two channel
systems are interconnected, wherein, however, the channel

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intersections are free of super cages and β-cages,
respectively, as well as free of α-cages. These super cages
and α-cages interconnecting the different channels have
diameters which are larger than those of the channels and
5   the apertures of the channels, respectively. Therefore, the
preferred embodiment of the invention, in which the solid
structure of the normally solid catalyst is free of super
cages further increases the shape-selectivity of the
transformation by further defining the catalyst.

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In accordance with the present invention, the normally
solid catalyst has preferably a Si/Al ratio of higher than
6, more preferably higher than 15. As indicated, the Si/Al
ratio is a criterion to distinguish different zeolites,
15   modified zeolites and zeolite-like materials. Moreover, the
Si/Al ratio strongly influences important properties of the
inventive solid catalyst. Thus, the preferred Si/Al ratio
indicated above leads to higher thermal and higher
hydrothermal stability of the inventive solid catalyst.
20   This is of particular benefit with respect to the
regeneration of the normally solid catalyst since water
might be formed during the regeneration process of the
catalyst and as a by-product in the inventive dielectric
barrier discharge reaction as well as small amounts of
25   carbon deposits and/or polymeric material and hydrocarbons
having a carbon chain built by 11 or more carbon atoms,
respectively.

The increased hydrothermal stability of the
30   aforementioned preferred embodiments of the present
invention thus minimizes and/or avoids damages to the solid
catalyst under the reaction conditions caused by the

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eventual formation of water. Moreover, the preferred Si/Al
ratio particularly contributes to the increase of the
structure destructive temperature of the inventive normally
solid catalysts allowing a standard regeneration taking

5   place at about 600°C. High silica Zeolite catalysts such as
HZSM-5 are thermally stable up to 1000°C.

Preferred normally solid catalysts having an at least
partially crystalline solid structure with at least one 10-

10   ring channel used in the present invention are a member of
the group selected from zeolites and modified zeolites
having a structure selected from FER, MEL, MFI, and MTT as
specified and defined in the above-mentioned "Atlas of
Zeolite Structure Types" reported by Meier and Olson in

15   Zeolites 17(1996), 1-230. Typical examples of those
preferred catalysts are the so-called pentasil-type
zeolites, such as Ferrierite and ZSM series catalysts, e.g.
ZSM-5, ZSM-23, ZSM-20 and ZSM-11, and the corresponding
modified zeolites as defined above. Preferred normally

20   solid catalysts having an at least partially crystalline
solid structure with at least one 12-ring channel used in
the present invention are a member of the group selected
from zeolites and modified zeolites having a structure
selected from BEA, LTL, MOR, and ZSM-12 as well as zeolite

25   M. Typical examples of those preferred catalysts are in
particular the zeolite Beta catalysts, and the
corresponding modified zeolites as defined above.

In particular the use of ZSM-5 zeolites on one hand,

30   and here preferably the NaZSM-5 and more preferably the
HZSM-5, and on the other hand, the use of zeolite Beta
catalysts, and here preferably the NaBeta and more

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preferably the HBeta, is highly preferred as the normally
solid catalyst for the present invention. The
shape-selective Zeolite ZSM-5 and Zeolite Beta,
respectively, are synthetic high-silica zeolites with a
5   high thermal stability. The MFI-type topology shows a
three-dimensional 10-member ring channel system having no
super cages in its structure; accordingly, the BEA-type
topology shows also a three-dimensional 12-member ring
channel system with no super cages in its structure.
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The use of a ZSM series zeolite catalyst and of Beta
zeolite catalysts for the inventive methods leads to a
product stream containing normally liquid hydrocarbons,
syngas, normally gaseous hydrocarbons, and higher
15   hydrocarbons, i.e. having a carbon chain of at least 11
carbon atoms (C>11), and/or polymeric material. The
products formed in the reaction over ZSM series and Beta
zeolite catalysts, respectively, particularly contain a
large amount of branched hydrocarbons having a carbon chain
20   of 6 to 10 and 6 to 9 carbon atoms, respectively, improving
the octane value and, thus, the quality of gasoline and
liquid fuel, respectively. Beneficial for these catalysts
are, moreover, the formation of some normally liquid
aromatics and oxygenates in the inventive methods. The
25   formation of polymer materials and higher hydrocarbons
(>C11) is strongly restricted over ZSM and Beta catalysts
because of their special pore structure and catalytic
properties.

30   The use of zeolite-like materials and, in particular,
the use of zeolites and modified zeolites as the normally
solid catalyst offers, moreover, the advantage of having

high concentrations of OH groups on the surfaces, i.e. on
the outer surfaces of the zeolite structure as well as
within the zeolite cavities and channels, respectively. In
addition to the high concentration of OH groups on zeolite

5   surfaces, an important characteristic of zeolites is the
natural coulombic field formed within the zeolite frame-
work. Within this context, it should be noted that both the
concentration of OH groups and the strength of the natural
coulombic field are controllable and adjustable. Generally,

10   these two features allow the zeolites to easily respond to
an external electric field, i.e. the zeolite becomes
electrically charged more easily. The control of the
dielectric barrier discharge according to the invention
allows though to control these charges and electrostatic

15   fields and, therefore, to control zeolite activity and
selectivity in the conversion of a normally gaseous
composition into a product stream containing at least a
normally liquid hydrocarbon.

20   As already indicated, the use of zeolite-like
materials, and in particular zeolites and modified
zeolites, as the normally solid catalyst inhibits the
formation of carbon black, in particular, the precipitation
of carbon black on the surface of the dielectric material,

25   thus, allowing a long term operation of the dielectric-
barrier discharge reactor. Moreover, the use of
aforementioned catalysts for the inventive method limits
the growth of the hydrocarbon chain. Consequently, an
increased yield of normally liquid hydrocarbons having a

30   normal boiling range of between about 50°C and about 210°C
results and the formation of higher hydrocarbons (C>11) and
polymeric material are suppressed. Furthermore, applying

shape-selective catalysts leads to an increased tendency to
form branched hydrocarbons, in particularly, of normally
liquid branched hydrocarbons representing a high-quality
fuel. Additionally, the function of the aforementioned
5   catalysts includes the chemisorption of methane and, thus,
the limitation of total decomposition of methane to carbon
and hydrogen.

A further advantage of zeolites is the possibility of a
10   controlled incorporation of acid centers in the
intracrystalline surface, e.g. during synthesis and/or by
subsequent ion exchange reaction. Thus, at temperatures
above 300°C, pentasils have acidities comparable to those
of mineral acids. Preferably, the normally solid catalyst
15   is an acid type zeolite catalyst, such as HZSM-5 or HBeta
with varying Si/Al ratios as described in Example 1 and
Example 2, respectively.

In further preferred embodiments of the invention, the
20   normally solid catalyst comprises at least one substance
selected from the group of metal ions and group IA, IIa,
IB, IIb and VIII elements of the periodic table. The latter
mentioned elements, i.e. alkali, earth alkali elements as
well as the elements of the zinc and the copper group and
25   the iron groups of the periodic table can be present either
in ionic or atomic form. Those normally solid catalysts are
synthesized by procedures generally known to the man skil-
led in the art, such as any type of ion exchange reactions
or impregnations, in case followed by subsequent thermal
30   activation or reduction. Examples of those solid catalysts
are the Fe-ZSM-5, Fe/H-ZSM-5, Mo/H-ZSM-5, and H-GaAlMFI for
catalysts having at least one 10-ring channel within its

structure, as well as the Fe-Beta, Fe/HBeta, and Mo/Hbeta
catalysts having at least one 12-ring channel within its
structure. The use of bifunctional catalysts, in particular
the introduction of an hydrogenation function in an acidic
5   zeolite, such as the incorporation of Pt^{2+} and Pd^{2+} ions may
further prevent or lower the formation of carbon deposits.

The normally liquid fuel obtainable by a dielectric
barrier discharge in accordance with the present invention
10   comprises at least 60 mol% of hydrocarbons, typically at
least 70 mol% of hydrocarbons, and preferably at least 80
mol% of hydrocarbons having a boiling range of between
about 50°C and about 210°C, typically between about 50°C and
about 180°C and a ratio branched hydrocarbons:linear hydro-
15   carbons of higher than 6:1, typically about 9:1. The nor-
mally liquid fuel generally contains less than 40 mol% of
oxygenated hydrocarbons, such as methanol, ethanol or
higher, typically branched oxygenates. Typically, the
normally liquid fuel comprises less than 30 mol% and
20   preferably less than 20 mol% of oxygenated hydrocarbons. In
particular, the selectivity towards methanol is generally
less than 2 mol%, typically less than 1 mol% and preferably
less than 0.5 mol%.

25   Further preferred embodiments of the present invention,
in particular, of the inventive apparatus are defined in
the sub-claims. Thus, a plurality of pairs of first and
second electrode means are arranged in an essentially
parallel or staked configuration forming a plurality of
30   discharge gaps, the gaps being connected in series to form
an elongated path for passage of said normally gaseous
composition.

Brief Description of the Drawings

For a better understanding of the nature and scope of
the present invention - and not to limit the invention -
preferred embodiments and details of the inventive method
and apparatus are described in more detail in the following
by reference to the drawings, in which:

Fig. 1 is a diagrammatic cross sectional view of a
preferred dielectric barrier discharge reactor configura-
tion according to the invention;

Fig. 2 is a diagrammatic cross sectional view of a
further preferred dielectric barrier discharge reactor
configuration according to the invention;

Detailed Description of the Drawings

The dielectric barrier discharge is a high pressure
non-equilibrium discharge which occurs when alternating
voltages are applied to a gas space between two electrodes
separated by a non-conducting medium. The amplitude of the
alternating high voltage has to be high enough to cause
electrical breakdown in the gas space. Fig. 1 shows schema-
tically a cross sectional view of a dielectric barrier
discharge reactor according to the invention. The high
voltage AC generator 1 is connected to the first electrode
2 and to the second grounded electrode 3 both having an es-
sentially cylindrical form. The electrodes are generally
made of corrosion-resistant metals or alloys or of materi-
als covered by at least one layer of an electrically con-

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ducting substance. Electrode 2 forms an inner shell and
Electrode 3 forms an outer shell. The dielectric layer 4 is
typically a glass, quartz or ceramic tube having a thick-
ness of between about 0.1 mm and about 5 mm and covers the

5   effective surface of electrode 2. The shape-selective
catalyst 5 shown in Fig. 1, is also formed in essentially
cylindrical form and is provided to cover the dielectric
layer 4. Typically, the dielectric tube 4 serves as support
for the solid catalyst 5. So, the solid catalyst 5, typi-

10   cally in powder form, is disposed in a piece of gas-perme-
able quartz fleece and wrapped around the outer surface of
the dielectric tube 4, i.e. the surface of the dielectric
tube 4 facing towards the electrode 3. Further catalyst
support arrangements preferably used for the present die-

15   lectric barrier discharge reaction are described in EP-
899'010 filed by the present assignee (the disclosure of
which being incorporated herein for all purposes by way of
reference). It is obvious that the form and the size of the
solid catalyst, i.e. whether it is applied in powder form

20   or as grains of different sizes and the manner by which the
catalyst is supported, i.e by means of the dielectric
material and by means of an additional support respective-
ly, can be modified within the scope of the present inven-
tion.

25

The normally gaseous composition passes in the axial
direction through the essentially annular discharge gap 6,
where it is exposed to the dielectric barrier discharge.
The dielectric barrier discharge is effected by an AC po-

30   tential applied between the first electrode and the second
electrode means. The preferred AC potential being in the
range of from about 6 kV to about 100 kV and the frequency

of the AC potential preferably being in the range of from
about 50 Hz to about 1 MHz. Generally a specific electric
power up to about 1-25 kW/m^2 of electrode area is fed into
the discharge reactor by automatically adjusting the

5   amplitude and frequency of the applied voltage. As
indicated above, an operating pressure in the range of from
about 0.01 bar to about 30 bar, preferably from about 0.1
bar to about 10 bar, at an operating temperature up to
about 400°C, preferably up to about 300°C, and more

10   preferably up to about 200°C, is maintained in the reactor.
The normally gaseous mixture is passed through said reactor
preferably at a flow rate of from about 0.1 m^3 per hour and
per m^2 of electrode area to about 10 m^3 per hour and per m^2
of electrode area.

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        When the amplitude of the applied AC electric field
reaches a critical value, breakdown is initiated in the gas
and a current flows from one electrode to the other. Once
breakdown is initiated at any location within the discharge

20   gap, charge accumulates on the dielectric leads to the
formation of an opposite electric field. This opposite
electric field reduces the external electric field within
the gap and interrupts the current flow in a few nanose-
conds to form short-lived microdischarges. The duration of

25   the current pulse relates to pressure and properties of
gases involved and the dielectrics applied. A large number
of such microdischarges will be generated when a
sufficiently high AC voltage is applied. The principal
advantages of dielectric barrier discharge are that non-

30   equilibrium plasma conditions are established at about
atmospheric pressure and that the entire electrode area is
effective for discharge reactions.

Fig. 2 shows another preferred configuration of a dielectric barrier discharge reactor according to the invention. The corresponding electrodes, the layer of the normally solid dielectric material and the normally solid catalyst respectively of this embodiment have or are arranged in an essentially planar form. Examples of the dielectric material are glass, as indicated, as well as quartz, ceramics, ZrO_2 or Al_2O_3.

Further preferred dielectric barrier discharge reactor configurations not being shown in the Figs. 1 and 2 are those, where the solid catalyst either occupies an essential part of the discharge gap 6 or where the solid catalyst covers only a portion of the dielectric material.

Examples

Example 1

The feed gases, i.e. a mixture containing methane and carbon dioxide, were introduced into the system flowing downstream through the reactor. The operative conditions were as follows (cf Table 1): Total flow rate (methane plus carbon dioxide) is 200 ml/min. The molar ratio of methane to carbon dioxide is 1:1. A temperature of 150°C, a pressure of 1 bar, and an electrical power of 500W are applied. The catalysts used are NaZSM-5(38), i.e. NaZSM-5 with a molar ratio of SiO_2/Al_2O_3 equal to 38, HZSM-5(38), HZSM-5(25) and NaY for comparison. A dielectric barrier discharge is thus initiated. A back pressure valve at the exit of the reactor was used to adjust the pressure. A MTI

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(Microsensor Technology Inc., M200H) dual-module micro gas
chromatograph containing a Poraplot Q column and a molecu-
lar sieve 5A-plot column with a TCD detector were used to
detect gaseous products. The gas sample was heated by a
5   heated line to avoid possible condensation before it was
taken into the gas chormatograph. The liquid sample was
analyzed by gas chromatography. The amount of higher
hydrocarbons (>C11) and polymer materials formed in the
dielectric barrier discharge reaction was determined by TGA
10   (Thermogravimetric analysis) measurement. The experiment
lasted for 300 min.

The operative conditions as well as the results
including the gas phase product distribution are reported
15   in Table 1, wherein the conversion of methane and carbon
dioxide respectively are defined as:

Conversion $[CH_4]$ = {$([CH_4]_{in} - [CH_4]_{out})/[CH_4]_{in}$} x 100%

20   and

Conversion $[CO_2]$ = {$([CO_2]_{in} - [CO_2]_{out})/[CO_2]_{in}$} x 100%

respectively. The selectivity of the products are defined
25   as:

Selectivity [prod.] =
{(number of carbon atoms of prod. x [prod.]$_{out}$)/total carbon
amount converted} x 100%

30

The analysis of the gas sample reveals formation of
carbon monoxide CO, alkanes having 2 to 4 carbon atoms (C2-

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C4) such as iso-butane, unsaturated hydrocarbons such as ethylene, small amount of oxygenated products such as methanol as well as water and hydrogen.

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Table 1.

Catalyst	NaY	NaZSM-5(38)	HZSM-5(38)	HZSM-5(25)
Reaction temperature (K)	423	423	423	423
Pressure (bar)	1	1	1	1
CH_4/CO_2 (molar ratio)	1	1	1	1
Flow rate (ml/min)	200	200	200	200
Reaction time (min)	300	300	300	300
Power applied (W)	500	500	500	500
Reagents in and out the reactor (g)				
CH_{4in}	21.43	21.43	21.43	21.43
Out	6.76	8.95	7.56	6.43
Conversion of CH_4 (wt%)	68.46	58.24	64.72	69.99
CO_{2in}	58.93	58.93	58.93	58.93
Out	35.21	38.41	36.70	32.97
Conversion of CO_2 (wt%)	40.25	34.82	37.72	44.05
Gas Product distribution (g)				
H_2	1.32	0.84	1.40	1.59
CO	16.65	16.47	18.09	19.27
C_2H_4	0.08	0.07	0.08	0.07
C_2H_6	2.00	1.96	2.00	1.95
C_3H_8	1.08	0.94	1.08	1.00
iso-C_4H_{10}	2.11	1.70	1.90	1.83
C_4H_8	0.20	0.25	0.17	0.24
C_4H_{10}	0.33	0.29	0.23	0.31
CH_3OH	0.04	0.05	0.06	0.06
H_2O	2.73	2.38	2.69	3.04
>C_5 and oxygenates and polymer material (g)*	11.86	8.05	8.38	11.58

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Table 2 shows the carbon number distribution in the organic liquid phase. The analysis of the liquid sample shows a high yield of gasoline components (C5-C11) being rich in branched hydrocarbons. In particular, the use of ZSM-5 series catalysts lead to a very high selectivity of C5 to C11 hydrocarbons, in particular of C6 to C10. As compared to NaZSM-5(38) the use of the acid-type catalyst HZSM-5(38) having the same Si/Al ratio shifts the selectivity towards longer chain formation and higher hydrocarbons within the aforementioned group, i.e. C5-C11 hydrocarbons. Similarly, a higher Si/Al ratio also shifts the selectivity towards the formation of longer chains and higher hydrocarbons, respectively, as indicated by the results of the inventive method obtained with HZSM-5(38) and HZSM-5(25) reported in Table 2.

Table 2. Carbon number distribution in liquid organic phase

	NaY	NaZSM-5(38)	HZSM-5(38)	HZSM-5(25)
Liquid product composition(wt%)				
C_3	17.86	0.12	0.16	0.24
C_4	40.51	3.40	1.76	6.13
C_5	27.66	7.99	4.99	13.82
C_6	1.65	18.62	12.54	26.68
C_7	10.21	19.29	10.93	14.70
C_8	1.44	17.51	20.58	15.00
C_9	0	24.37	24.21	16.56
C_{10}	0	7.48	19.78	5.58
C_{11}	0.68	1.17	4.91	0.93

Table 3. Product distribution in liquid organic phase

	NaY	NaZSM-5(38)	HZSM-5(38)	HZSM-5(25)
<ins>Liquid product distribution(wt%)</ins>				
Paraffins	16.80	52.39	34.02	56.99
Aromatics	0	5.57	8.27	3.28
Naphthenes**	0.54	31.09	39.03	25.56
Unknowns	82.66	10.95	18.68	14.17

** alicyclic compounds; term often used in the petrochemistry

5

Table 4. TGA Analysis Results

	NaY	NaZSM-5(38)	HZSM-5(25)
Pore structure	Three dimensional with interlinking channels	Bidimensional with large intersection (straight and sinusoidal)	Bidimensional with large intersection (straight and sinusoidal)
Pore Size (Å)	7.4(supercage)	5.4*5.6	5.4*5.6
Weight loss(wt%)	39.5	21.4	15.8
Polymer(>C_{11}) formed(g)*	1.58	0.85	0.63

* after reaction for 300 min.

10

Table 4 shows the results of the TGA analysis after the
inventive dielectric barrier discharge reaction of 300 min.
The higher weight loss observed in the case of NaY
15   indicates that, first, NaY has a poorer thermal stability
as compared to the ZSM-5 series catalysts NaZSM-5 and HZSM-
5, and, second, the use of NaY as the normally solid
catalyst for the inventive method leads to much higher

amounts of polymeric material or higher hydrocarbons (>C11)
as compared to NaZSM-5 and HZSM-5.

5   **Example 2**

       The feed gases, i.e. a mixture containing methane and
       carbon dioxide, were introduced into the system flowing
       downstream through the reactor. The operative conditions
10   were as follows (cf Table 5): Total flow rate (methane plus
       carbon dioxide) is 200 ml/min. The molar ratio of methane
       to carbon dioxide is 1:1. A temperature of 150°C, a
       pressure of 1 bar, and an electrical power of 500W are
       applied. The catalysts used are NaBeta, HBeta and NaY for
15   comparison. A dielectric barrier discharge is thus initia-
       ted. A back pressure valve at the exit of the reactor was
       used to adjust the pressure. A MTI (Microsensor Technology
       Inc., M200H) dual-module micro gas chromatograph containing
       a Poraplot Q column and a molecular sieve 5A-plot column
20   with a TCD detector were used to detect gaseous products.
       The gas sample was heated by a heated line to avoid
       possible condensation before it was taken into the gas
       chormatograph. The liquid sample was analyzed by gas
       chromatography. The amount of higher hydrocarbons (>C11)
25   and polymer materials formed in the dielectric barrier
       discharge reaction was determined by TGA (Thermogravimetric
       analysis) measurement. The experiment lasted for 300 min.

       The operative conditions as well as the results
30   including the gas phase product distribution are reported
       in Table 5, wherein the conversion of methane and carbon

30

dioxide as well as the selectivity of the products are
defined as indicated in Example 1.

The analysis of the gas sample reveals formation of
carbon monoxide CO, alkanes having 2 to 4 carbon atoms (C2-
C4) such as iso-butane, unsaturated hydrocarbons such as
ethylene, small amount of oxygenated products such as
methanol as well as water and hydrogen. In particular, the
use of HBeta as the normally solid catalyst leads to a high
conversion and yield with respect to normally liquid
compounds, particularly, to normally liquid hydrocarbons.
Thus, Hbeta is highly preferred as the normally solid
catalyst due to its high activity in the inventive method.

Table 5.

Catalyst	NaY	NaBeta	Hbeta
Reaction temperature (K)	423	423	423
Pressure (bar)	1	1	1
CH_4/CO_2 (molar ratio)	1	1	1
Flow rate (ml/min)	200	200	200
Reaction time (min)	300	300	300
Power applied (W)	500	500	500
Reagents in and out the reactor (g)			
CH_{4in}	21.43	21.43	21.43
Out	6.76	7.68	5.51
Conversion of CH_4 (wt%)	68.46	64.16	74.29
CO_{2in}	58.93	58.93	58.93
Out	35.21	36.52	33.46
Conversion of CO_2 (wt%)	40.25	38.03	43.22
Gas Product distribution (g)			
H_2	1.32	1.36	1.69
CO	16.65	18.09	17.72
C_2H_4	0.08	0.06	0.07
C_2H_6	2.00	1.97	1.94
C_3H_8	1.08	0.95	1.00
$iso\text{-}C_4H_{10}$	2.11	1.43	1.40
C_4H_8	0.20	0.00	0.21
C_4H_{10}	0.33	0.20	0.29
CH_3OH	0.04	0.07	0.07
H_2O	2.73	3.13	3.36
$>C_5$ and oxygenates and polymer material (g)*	11.86	8.89	13.65

Table 6 shows the carbon number distribution in the
organic liquid phase. The analysis of the liquid sample
shows a high yield of gasoline components (C5-C11) being
5   rich in branched hydrocarbons. In particular, the use of
HBeta leads to a very high selectivity of C5 to C11
hydrocarbons, in particular of C6 to C9.

10   Table 6. Carbon number distribution in liquid organic phase

	NaY	NaBeta	HBeta
Liquid product composition(wt%)			
C_3	17.86	0.21	0.94
C_4	40.51	2.81	3.02
C_5	27.66	8.23	8.61
C_6	1.65	17.19	17.63
C_7	10.21	15.81	24.82
C_8	1.44	17.61	18.04
C_9	0	21.78	15.73
C_{10}	0	13.22	8.30
C_{11}	0.68	3.07	2.85
C_{12}	0	0.07	0.07

Table 7 shows the product distribution in the liquid
organic phase classified in the different types of
15   hydrocarbons formed. Hbeta as the normally solid catalyst
results in a high yield and formation, respectively, of
paraffins.

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Table 7. Product distribution in liquid organic phase

	NaY	NaBeta	HBeta
Liquid product distribution(wt%)			
Paraffins	16.80	44.19	55.15
Aromatics	0	6.37	6.98
Naphthenes**	0.54	30.84	8.82
Unknowns	82.66	18.60	29.05

** alicyclic compounds; term often used in the petrochemistry

Table 8. Characteristics of the Zeolites Used and
          TGA Analysis Results

	NaY	NaBeta	HBeta
Channel structure	Three dimensional with interlinking channels	Three dimensional with interlinking channels	Three dimensional with interlinking channels
Pore Size (Å)	7.4(supercage)	5.5*5.5 7.6*6.4	5.5*5.5 7.6*6.4
Crystal Size	1.0 μm	0.5 μm	0.5 μm
SiO_2/Al_2O_3 (molar ratio)	4.7	38	38
Weight loss(wt%)	39.51	28.30	29.12
Polymer($>C_{11}$) formed(g)*	1.58	1.13	1.16

* after reaction for 300 min.

Table 8 shows the characteristics of the zeolites used
in this Example and the results of the TGA analysis after
the inventive dielectric barrier discharge reaction of 300

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min. The higher weight loss observed in the case of NaY indicates that, first, NaY has a poorer thermal stability as compared to the zeolite Beta catalysts NaBeta and HBeta, and, second, the use of NaY as the normally solid catalyst for the inventive method leads to much higher amounts of polymeric material or higher hydrocarbons (>C11) as compared to NaBeta and HBeta.

The success in the research and development of a feasible utilization of greenhouse gases, in particular methane and carbon dioxide, which led to the present invention signify the attainment of two important objectives: First, slowing down a build-up of greenhouse gases in the atmosphere and, second, better carbon resource utilization. An extra advantage of such an utilization of these major greenhouse gases is the fact that such synthesized liquid fuel does not contain pollutants like sulfur that are usually present in coal and petroleum.

Although certain preferred embodiments of the invention have been described herein, it will be apparent to those skilled in the art to which the invention pertains that modifications and variations of the described embodiments may be made without departing from the spirit and scope of the invention.

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List of Reference Signs

1   high voltage AC generator

2   first electrode means

5   3   second electrode means

4   dielectric layer, dielectric material

5   catalyst

6   discharge gap

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Claims:

1. A method of transforming a normally gaseous composition
containing carbon dioxide and at least one normally gaseous
hydrocarbon into a product stream containing at least one
normally liquid hydrocarbon; said method comprising the
steps of:
        feeding said composition into a reactor including a
first electrode means, a second electrode means and at
least one layer of a normally solid dielectric material
positioned between said first and said second electrode
means;
        submitting said composition within said reactor in the
presence of a normally solid catalyst to a dielectric
barrier discharge, wherein said normally solid catalyst is
a member selected from the group of zeolites, modified
zeolites and zeolite-like materials, and wherein said
normally solid catalyst has an at least partially
crystalline solid structure with at least one 10-ring
channel; and
        controlling said dielectric barrier discharge to
convert said normally gaseous composition into said product
stream.

2. The method of claim 1 wherein said at least one
normally gaseous hydrocarbon is selected from the group of
methane, ethane and propane.

3. The method of claim 1 or 2 wherein said at least one
normally gaseous hydrocarbon is methane.

4.   The method of claim 2 or 3 wherein said carbon dioxide
and said methane are contained in said normally gaseous
composition at a molar ratio of carbon dioxide:methane of
between about 1:1 to about 1:4, preferably between about
5   1:2 to about 1:3. he

5.   The method of any of claims 1 to 4 wherein said at
least one 10-ring channel has a diameter of between about 4
Å and about 7 Å.
10

6.   The method of any of claims 1 to 5 wherein said solid
structure of said normally solid catalyst is free of super
cages.

15   7.   The method of any of claims 1 to 6 wherein said
normally solid catalyst has a Si/Al ratio of higher than 6,
preferably higher than 15.

8.   The method of any of claims 1 to 7 wherein said
20   normally solid catalyst is a zeolite or a modified zeolite
having a crystalline solid structure selected from FER,
MEL, MFI, and MTT.

9.   The method of any of claims 1 to 8 wherein said
25   normally solid catalyst comprises at least one substance
selected from the group of metal ions and group IA, IIa,
IB, IIb and VIII elements of the periodic table.

10. A method of transforming a normally gaseous composition
30   containing carbon dioxide and at least one normally gaseous
hydrocarbon into a product stream containing at least one

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normally liquid hydrocarbon; said method comprising the
steps of:

  feeding said composition into a reactor including a
first electrode means, a second electrode means and at
5   least one layer of a normally solid dielectric material
positioned between said first and said second electrode
means;

  submitting said composition within said reactor in the
presence of a normally solid catalyst to a dielectric
10 barrier discharge, wherein said normally solid catalyst is
a member selected from the group of zeolites, modified
zeolites and zeolite-like materials, and wherein said
normally solid catalyst has an at least partially
crystalline solid structure with at least one 12-ring
15 channel; and

  controlling said dielectric barrier discharge to
convert said normally gaseous composition into said product
stream.

20 11. The method of claim 10 wherein said at least one
normally gaseous hydrocarbon is selected from the group of
methane, ethane and propane.

12. The method of claim 10 or 11 wherein said at least one
25 normally gaseous hydrocarbon is methane.

13. The method of claim 11 or 12 wherein said carbon
dioxide and said methane are contained in said normally
gaseous composition at a molar ratio of carbon
30 dioxide:methane of between about 1:1 to about 1:4, pre-
ferably between about 1:2 to about 1:3.

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14. The method of any of claims 10 to 13 wherein said at least one 12-ring channel has a diameter of between about 4 Å and about 8 Å.

5   15. The method of any of claims 10 to 14 wherein said solid structure of said normally solid catalyst is free of super cages.

16. The method of any of claims 10 to 15 wherein said
10 normally solid catalyst has a Si/Al ratio of higher than 6, preferably higher than 15.

17. The method of any of claims 10 to 16 wherein said normally solid catalyst is a zeolite or a modified zeolite
15 having a crystalline solid structure selected from BEA, LTL, MOR, and ZSM-12.

18. The method of any of claims 10 to 17 wherein said normally solid catalyst comprises at least one substance
20 selected from the group of metal ions and group IA, IIa, IB, IIb and VIII elements of the periodic table.

19. A normally liquid fuel obtainable by a dielectric bar-rier discharge, said normally liquid fuel comprising at
25 least 60 mol% of hydrocarbons having a normal boiling range of between about 50°C and about 210°C, and less than 40 mol% of oxygenated hydrocarbons.

20. An apparatus for transforming a normally gaseous compo-
30 sition containing carbon dioxide and at least one normally gaseous hydrocarbon into a product stream containing at

least one normally liquid hydrocarbon; said apparatus comprising:

a dielectric barrier discharge reactor including a first electrode means, a second electrode means and at least one layer of a normally solid dielectric material positioned between said first and said second electrode means;

means for applying an AC potential between said first and said second electrode means;

means for feeding said composition into said reactor;

a normally solid catalyst arranged for contact with said gaseous composition when subjected to said dielectric barrier discharge, wherein said normally solid catalyst is a member selected from the group of zeolites, modified zeolites and zeolite-like materials, and wherein said normally solid catalyst has an at least partially crystalline solid structure with at least one 10-ring channel; and

means for controlling said dielectric barrier discharge to convert said normally gaseous composition into said product stream.

21. The apparatus of claim 20 wherein said at least one normally gaseous hydrocarbon is selected from the group of methane, ethane and propane, preferably said at least one normally gaseous hydrocarbon being methane.

22. The apparatus of claim 21 wherein said carbon dioxide and said methane are contained in said normally gaseous composition at a molar ratio of carbon dioxide:methane of between about 1:1 to about 1:4, preferably between about 1:2 to about 1:3.

23. The apparatus of any of claims 20 to 22 wherein said at least one 10-ring channel has a diameter of between about 4 Å and about 7 Å.

24. The apparatus of any of claims 20 to 23 wherein said solid structure of said normally solid catalyst is free of super cages.

25. The apparatus of any of claims 20 to 24 wherein said normally solid catalyst has a Si/Al ratio of higher than 6, preferably higher than 15.

26. The apparatus of any of claims 20 to 25 wherein said normally solid catalyst is a zeolite or a modified zeolite having a crystalline solid structure selected from FER, MEL, MFI, and MTT.

27. The apparatus of any of claims 20 to 26 wherein said normally solid catalyst comprises at least one substance selected from the group of metal ions and group IA, IIa, IB, IIb and VIII elements of the periodic table.

28. An apparatus for transforming a normally gaseous composition containing carbon dioxide and at least one normally gaseous hydrocarbon into a product stream containing at least one normally liquid hydrocarbon; said apparatus comprising:
      a dielectric barrier discharge reactor including a first electrode means, a second electrode means and at least one layer of a normally solid dielectric material

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positioned between said first and said second electrode means;

means for applying an AC potential between said first and said second electrode means;

5   means for feeding said composition into said reactor;

a normally solid catalyst arranged for contact with said gaseous composition when subjected to said dielectric barrier discharge, wherein said normally solid catalyst is a member selected from the group of zeolites, modified

10   zeolites and zeolite-like materials, and wherein said normally solid catalyst has an at least partially crystalline solid structure with at least one 12-ring channel; and

means for controlling said dielectric barrier discharge

15   to convert said normally gaseous composition into said product stream.

29. The apparatus of claim 28 wherein said at least one normally gaseous hydrocarbon is selected from the group of

20   methane, ethane and propane, preferably said at least one normally gaseous hydrocarbon being methane.

30. The apparatus of claim 29 wherein said carbon dioxide and said methane are contained in said normally gaseous

25   composition at a molar ratio of carbon dioxide:methane of between about 1:1 to about 1:4, preferably between about 1:2 to about 1:3.

31. The apparatus of any of claims 28 to 30 wherein said at

30   least one 12-ring channel has a diameter of between about 4 Å and about 8 Å.

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32. The apparatus of any of claims 28 to 31 wherein said solid structure of said normally solid catalyst is free of super cages.

5   33. The apparatus of any of claims 28 to 32 wherein said normally solid catalyst has a Si/Al ratio of higher than 6, preferably higher than 15.

34. The apparatus of any of claims 28 to 33 wherein said
10   normally solid catalyst is a zeolite or a modified zeolite having a crystalline solid structure selected from BEA, LTL, MOR, and ZSM-12.

35. The apparatus of any of claims 28 to 34 wherein said
15   normally solid catalyst comprises at least one substance selected from the group of metal ions and group IA, IIa, IB, IIb and VIII elements of the periodic table.
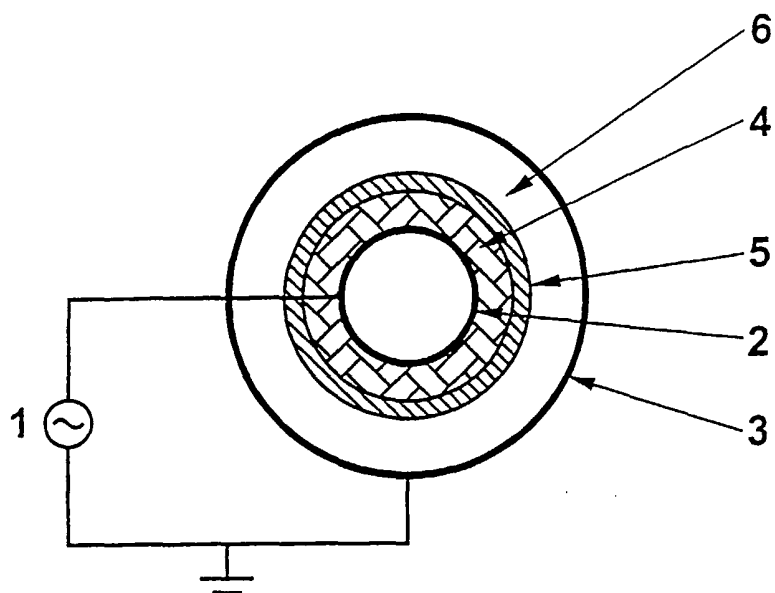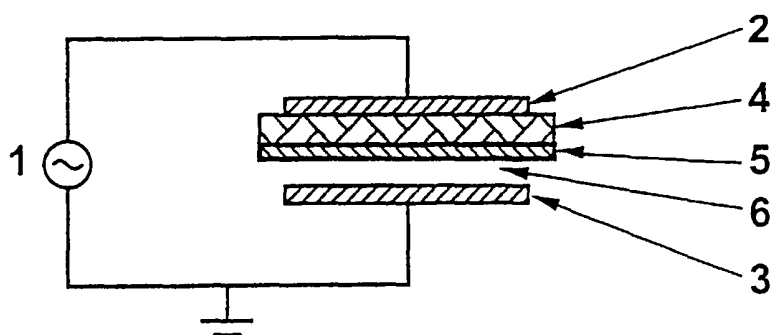
FIG. 1

FIG. 2

INTERNATIONAL SEARCH REPORT

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7   C07C2/86   B01J19/08

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 7   C07C   B01J

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

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

EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	DE 42 20 865 A (ASEA BROWN BOVERI) 18 February 1993 (1993-02-18) claims 1,7,11 figures 1-3 --- -/--	1,2,5, 7-11, 16-18, 20,21, 23, 25-30, 33-35

X	Further documents are listed in the continuation of box C.		X	Patent family members are listed in annex.

° Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

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"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

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"P" document published prior to the international filing date but later than the priority date claimed

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

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

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Date of the actual completion of the international search	Date of mailing of the international search report
4 December 2000	13/12/2000

Name and mailing address of the ISA	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL – 2280 HV Rijswijk Tel. (+31–70) 340-2040, Tx. 31 651 epo nl, Fax: (+31–70) 340-3016	De Herdt, O

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INTERNATIONAL SEARCH REPORT

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

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