



# PATENT COOPERATION TREATY

## PCT

### INTERNATIONAL PRELIMINARY REPORT ON PATENTABILITY

(Chapter II of the Patent Cooperation Treaty)

(PCT Article 36 and Rule 70)

Applicant's or agent's file reference 10141-WO-PCT	<b>FOR FURTHER ACTION</b> See Form PCT/IPEA/416	
International application No. PCT/EP2006/006225	International filing date ( <i>day/month/year</i> ) 22.06.2006	Priority date ( <i>day/month/year</i> ) 06.07.2005
International Patent Classification (IPC) or national classification and IPC INV. C07C2/82		
Applicant Saudi Basic Industries Corporation		
<p>1. This report is the international preliminary examination report, established by this International Preliminary Examining Authority under Article 35 and transmitted to the applicant according to Article 36.</p> <p>2. This REPORT consists of a total of <u>6</u> sheets, including this cover sheet.</p> <p>3. This report is also accompanied by ANNEXES, comprising:</p> <p>a. <input checked="" type="checkbox"/> <i>sent to the applicant and to the International Bureau</i> a total of <u>2</u> sheets, as follows:</p> <p style="margin-left: 20px;"><input checked="" type="checkbox"/> sheets of the description, claims and/or drawings which have been amended and are the basis of this report and/or sheets containing rectifications authorized by this Authority (see Rule 70.16 and Section 607 of the Administrative Instructions).</p> <p style="margin-left: 20px;"><input type="checkbox"/> sheets which supersede earlier sheets, but which this Authority considers contain an amendment that goes beyond the disclosure in the international application as filed, as indicated in item 4 of Box No. I and the Supplemental Box.</p> <p>b. <input type="checkbox"/> (<i>sent to the International Bureau only</i>) a total of (indicate type and number of electronic carrier(s)) , containing a sequence listing and/or tables related thereto, in electronic form only, as indicated in the Supplemental Box Relating to Sequence Listing (see Section 802 of the Administrative Instructions).</p>		
<p>4. This report contains indications relating to the following items:</p> <p><input checked="" type="checkbox"/> Box No. I Basis of the report</p> <p><input type="checkbox"/> Box No. II Priority</p> <p><input type="checkbox"/> Box No. III Non-establishment of opinion with regard to novelty, inventive step and industrial applicability</p> <p><input type="checkbox"/> Box No. IV Lack of unity of invention</p> <p><input checked="" type="checkbox"/> Box No. V Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement</p> <p><input type="checkbox"/> Box No. VI Certain documents cited</p> <p><input type="checkbox"/> Box No. VII Certain defects in the international application</p> <p><input type="checkbox"/> Box No. VIII Certain observations on the international application</p>		
Date of submission of the demand  2007-04-16	Date of completion of this report  06.11.2007	
Name and mailing address of the international preliminary examining authority:   European Patent Office - P.B. 5818 Patentlaan 2 NL-2280 HV Rijswijk - Pays Bas Tel. +31 70 340 - 2040 Tx: 31 651 epo nl Fax: +31 70 340 - 3016	Authorized officer  O'Sullivan, Paul  Telephone No. +31 70 340-4511  	

**INTERNATIONAL PRELIMINARY REPORT  
ON PATENTABILITY**

International application No.  
PCT/EP2006/006225

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**Box No. I Basis of the report**

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1. With regard to the **language**, this report is based on

- the international application in the language in which it was filed
- a translation of the international application into , which is the language of a translation furnished for the purposes of:
  - international search (under Rules 12.3(a) and 23.1(b))
  - publication of the international application (under Rule 12.4(a))
  - international preliminary examination (under Rules 55.2(a) and/or 55.3(a))

2. With regard to the **elements\*** of the international application, this report is based on (*replacement sheets which have been furnished to the receiving Office in response to an invitation under Article 14 are referred to in this report as "originally filed" and are not annexed to this report*):

**Description, Pages**

1, 2, 4-14	as originally filed
3, 3a	received on 16.04.2007 with letter of 13.04.2007

**Claims, Numbers**

1-16	as originally filed
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- a sequence listing and/or any related table(s) - see Supplemental Box Relating to Sequence Listing

3.  The amendments have resulted in the cancellation of:

- the description, pages
- the claims, Nos.
- the drawings, sheets/figs
- the sequence listing (*specify*):
- any table(s) related to sequence listing (*specify*):

4.  This report has been established as if (some of) the amendments annexed to this report and listed below had not been made, since they have been considered to go beyond the disclosure as filed, as indicated in the Supplemental Box (Rule 70.2(c)).

- the description, pages
- the claims, Nos.
- the drawings, sheets/figs
- the sequence listing (*specify*):
- any table(s) related to sequence listing (*specify*):

\* *If item 4 applies, some or all of these sheets may be marked "superseded."*

**INTERNATIONAL PRELIMINARY REPORT  
ON PATENTABILITY**

International application No.  
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**Box No. V Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement**

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1. Statement

Novelty (N)	Yes: Claims	<u>1-16</u>
	No: Claims	
Inventive step (IS)	Yes: Claims	<u>1-16</u>
	No: Claims	
Industrial applicability (IA)	Yes: Claims	<u>1-16</u>
	No: Claims	

2. Citations and explanations (Rule 70.7):

**see separate sheet**

**Re: Item V**

Reference is made to the following documents; the numbering will be adhered to in the rest of the procedure:

- D1: US-A-5 270 016 (ALAGY ET AL) 14 December 1993 (1993-12-14)
- D2: US-A-4 726 913 (BROPHY ET AL) 23 February 1988 (1988-02-23)
- D3: 1983-755483 (WPI abstract)
- D4: US-A-5 824 834

**Novelty (Art 33(2) PCT)**

D1 discloses an apparatus for thermal conversion of methane to hydrocarbons of higher molecular weight. In example 2 of D1, it can be seen that the main products, apart from hydrogen and methane starting material, are acetylene and ethylene. In one embodiment of D1, it is noted that direct quenching of the effluent may be carried out. The effluent from the reactor is cooled very rapidly by putting it into direct contact with cooling fluid which may be chosen from liquified petroleum gases, propane, hydrocarbon oils or water. According to D1, 'Propane is the preferred quenching gas, since it can also be partially cracked and thus contribute to the formation of products such as ethylene'. Thus it is clear said in D1 that adding alkanes such as propane to the acetylene effluent lead to the formation of products such as ethylene. However, D1 does not disclose the conversion of acetylene into ethylene by intimately mixing the acetylene containing effluent with an ethane feed as required by claim 1. Claims 1-16 may therefore be considered novel over D2.

D2 discloses a process for the production of synthesis gas and hydrocarbons (D1, column 1, lines 49-60) (note syn gas is necessarily produced in the conversion of methane to acetylene, see application page 9, second paragraph). Methane may be used as feed (column 2, line 7). Preferred products are acetylene, ethylene, higher olefins, aromatics and synthesis gas (column 2, lines 59-63). It is mentioned on column 3, lines 10-17 that: " .. an alternative mode of quench is envisaged if it is required to increase the amount of unsaturated hydrocarbons in the product gases. This mode comprises the injection of, for example, a liquid saturated hydrocarbon e.g. propane, butane or gasoline, into the hot product gases and to thereby increase the content of light unsaturated hydrocarbons, e.g. ethylene, acetylene in the product gases". However, D2 does not disclose the conversion of acetylene into ethylene by intimately mixing the acetylene containing effluent with an ethane feed as required by claim 1.

Claims 1-16 may therefore be considered novel over D2.

D3 does not disclose the conversion of a feed charge containing methane to acetylene.

D4 does not disclose the production of ethylene from acetylene and ethane.

**Inventive Step (Art 33(3) PCT)**

1. The difference between D1 and the present claims is that D1 does not disclose the conversion of acetylene into ethylene by intimately mixing the acetylene containing effluent with an ethane feed, although D1 (see table column 15) does result in the production of ethylene. D1 does disclose (column 6, lines 27-37) that the product of the reaction which contains acetylene may be quenched using propane as the preferred quenching gas, since it can also be partially cracked and thus contribute to the formation of products such as ethylene. The problem underlying the present application may therefore be considered as the provision of an alternative process for the production of ethylene. It is not clear from the disclosure of D1 whether propane reacts directly with acetylene to produce ethylene and propylene or whether propane is merely cracked to produce products such as ethylene without reacting with the product acetylene. Even should the propane react with acetylene, it is not exclusively the desired ethylene that results. Therefore the skilled person looking for an alternative to the process of D1 would not be given any incentive to make the changes to the process resulting in the presently claimed embodiments. Claims 1-16 are therefore considered inventive over D1.

2. Novelty of the present claims with respect to D2 is discussed above. It is mentioned in D2, column 3, lines 10-17 that: " .. an alternative mode of quench is envisaged if it is required to increase the amount of unsaturated hydrocarbons in the product gases. This mode comprises the injection of, for example, a liquid saturated hydrocarbon e.g. propane, butane or gasoline, into the hot product gases and to thereby increase the content of light unsaturated hydrocarbons, e.g. ethylene, acetylene in the product gases". The fact that the addition of saturated hydrocarbons is presumed to increase the content of light unsaturated hydrocarbons *including* acetylene is something which would point the skilled person away from the teaching of D2 should he be seeking an alternative process for the production of ethylene. Present claims 1-16 are therefore considered inventive over D2.

3. D3 may be considered as the closest prior art since it discloses a process for the

conversion of acetylene and ethane into ethylene (examples, second paragraph). This reaction is carried out thermally in the absence of a catalyst. The difference between D3 and the present claims is that D3 does not disclose the first step of the process, the conversion of methane to acetylene, nor does it disclose that pyrolysis/hydrogenation to produce ethylene takes place in situ. Example 1 of the present invention demonstrates an acetylene conversion of higher than 90% obtained by in situ hydrogenation, by adding ethane to a pyrolysis product gas containing syngas, acetylene and water (p 10-11; table 1). In D3 (table 1) a maximum of 70.6% acetylene conversion is obtained using a more complicated process involving intermediate purification steps. The problem is therefore the provision of an improved process for acetylene conversion. Neither D3 nor any of the other prior art provide a suggestion for the skilled person that the problem may be solved by performing an in situ hydrogenation. The present claims must therefore be considered inventive.

16.04.2007

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complicates the process design in addition to the limited specific production rate due to the acetylene solubility in the solvent.

Deactivation of Pd-containing catalysts by green oil during acetylene hydrogenation was also described in scientific literature (R.K. Edvinsson, A.M. Holmgren and S. Irandoust, *Ind. Eng. Chem. Res.* 1995, 34, 94-100). These authors suggested that a special type of monolith reactor can be used for the gas/liquid/solid acetylene hydrogenation reaction. In that work, acetylene hydrogenation was carried out in the presence of Pd/ $\alpha$ -Al<sub>2</sub>O<sub>3</sub> on the surface of monolithic support in the liquid phase at 40°C and 20 atm pressure with using 3% C<sub>2</sub>H<sub>2</sub> + 28% C<sub>2</sub>H<sub>4</sub> + 6% to 11% H<sub>2</sub> + N<sub>2</sub> (balance) mixture. The selectivity to ethylene dropped significantly with the increase of C<sub>2</sub>H<sub>2</sub> conversion. At 90% of C<sub>2</sub>H<sub>2</sub> conversion, the selectivity of C<sub>2</sub>H<sub>2</sub> to ethylene was found to be 60%. Nevertheless, the catalyst was not stable in continuous experiments. After 50 hours, the selectivity to ethylene started to decrease. It was also indicated that the influence of the presence of CO in the gas feed mixture was detrimental to the catalyst rate of hydrogenation; at 2400 ppm of CO the hydrogenation reaction stopped completely. The reduction of hydrogenation rate was attributed to CO blocking some of the hydrogen adsorption sites. Clearly it is a must to include a CO purification step in a traditional catalytic hydrogenation process.

A similar concept of catalytic hydrogen transfer was mentioned and practiced in prior art at quiet different reaction conditions (US 3,267,170 and US 3,321,545). However, the performance pertaining to such a reaction is still constrained by catalyst activity and selectivity. This also requires a separate hydrogen transfer reactor downstream, and requires a prior gas-purification step.

Publication JP58-126819A discloses a non-catalytic process of acetylene conversion to ethylene. The product obtained by pyrolysis of ethane and naphtha is first separated in a C2 fraction and other fractions (C1, C3, C4 etc.). The C2 fraction (acetylene, ethylene, and ethane) is then introduced into an acetylene separation zone, from where pure acetylene is recovered. The pure acetylene obtained is subsequently diluted with ethane in a separate process unit and subjected to pyrolysis. A maximum of 70.6% acetylene conversion is provided. This process is rather complicated, as

ethylene is obtained from acetylene in a sequence of purification steps before reduction with ethane.

### Summary Of The Invention

5           The known processes for producing ethylene from a methane-containing feed show several disadvantages, like catalyst deactivation, deep hydrogenation, green oil or carbon formation, temperature runaway problems, or a low production rate per unit reactor volume. There is thus a need in industry for an improved process, especially allowing more efficient and stable hydrogenation of acetylene into ethylene..

10           The present invention provides such an improved process for the production of ethylene, which process comprises the steps of

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