(19) Europäisches Patentamt
European Patent Office
Office européen des brevets

(11) EP 1 657 290 A1

(12) EUROPEAN PATENT APPLICATION

(43) Date of publication:
17.05.2006 Bulletin 2006/20

(51) Int Cl.:
C10G 2/00 *(2006.01)* ***C07C 1/04*** *(2006.01)*

(21) Application number: **04105668.0**

(22) Date of filing: **10.11.2004**

(84) Designated Contracting States:
AT BE BG CH CY CZ DE DK EE ES FI FR GB GR HU IE IS IT LI LU MC NL PL PT RO SE SI SK TR
Designated Extension States:
AL HR LT LV MK YU

(71) Applicant: **Research Institute of Petroleum Industry**
18799 Teheran (IR)

(72) Inventors:
- **Zamani, Yahya**
  3rd Floor, No.16, Kalantary
  Street Abouzar sqare,
  Tehran (IR)
- **Pour, Ali Nakhaei**
  First Floor, No.4
  Khoshnevisan
  Alley, Azadi Square
  Tehran (IR)
- **Jozani, Kheirollah Jafari**
  Mahdi Street
  Karaj (IR)
- **Mehr, Jafar Yeganeh**
  Street,Kaj
  Street,Azimeieh
  Karaj (IR)

(74) Representative: **KEIL & SCHAAFHAUSEN**
Patentanwälte
Cronstettenstrasse 66
60322 Frankfurt am Main (DE)

(54) New catalyst for use during a single-stage gasoline production process from syngas and an improved process for regeneration of the same catalyst

(57) The present invention relates to a new and advantageous catalyst for use during a single-stage gasoline production process from syngas and a process making use of the same. During the process according to the invention, the catalyst can be recycled in an easy manner without stopping the process. Such a process is more economic and still further leads to constant octane numbers of the product at values of about 95. The new process prevents the catalyst from deactivation and increases its capacity, resulting in better conversion rates, becoming even better after each recycling step. Also, with the process according to the invention the catalyst's lifetime is significantly prolonged, making the whole process more economic.

Printed by Jouve, 75001 PARIS (FR)

Description

[0001] The present invention relates to a new and advantageous catalyst for use during a single-stage Gasoline production process from syngas and a process making use of the same. During the process according to the invention, the catalyst can be regenerated in an easy manner without stopping the process. Such a process is more economic and still further leads to constant octane numbers of the product at values of about 95. The new process prevents the catalyst from deactivation and increases its capacity, resulting in better conversion rates, becoming even better after each regeneration step. Also, with the process according to the invention the catalyst's lifetime is significantly prolonged, making the whole process more economic.

[0002] Two German scientists called Fischer and Tropsch, in 1920, first discovered a process for conversion of carbon monoxide and hydrogen to hydrocarbons. The catalysts used in such processes contain catalytically active metals of the transition elements VIII group of the periodic table However, in order to catalyze the conversion process of the syngas to hydrocarbons having five carbon atoms, metals like Fe, Co, Ni and Ru are more suitable.

[0003] The Fischer-Tropsch (FT) process was first commercially applied in 1930, in Germany, where, using a cobalt catalyst together with a promoter in a fixed bed reactor, more than 10000 barrels of hydrocarbons were daily produced.

[0004] Fischer and Pichler reported *inter alia* about their work in the German patent 731295 in 1936.

[0005] After the Second World War, a lot of efforts were made as to development and use of different catalysts useful in the FT process and different kind of reactors were built around the world. Since the FT process was discovered and established, the one major subject for research work for improving the process was to avoid deactivation of cobalt (Co) and iron (Fe) based catalysts during the process. Namely, with running such processes the problem appears that after a certain time catalyst is deactivated and hence its activity is reduced to such an extend that the whole production process becomes uneconomical. The catalyst must be replaced or regenerated, and due to the fact that the catalyst is one expensive materials used in the process, regeneration processes gained most attention.

[0006] Identification of factors that lead to catalyst deactivation is an important tool for achieving a better stability and life time of the catalyst. Also, methods for regeneration of the catalyst gained some attention.

[0007] One of the most important factor in deactivation of iron based catalysts is their contact with sulphur containing compounds, which appear during the process. In connection with water, which is a product of the process, the active sites of the catalyst are modified leading to inactivity of the same. Also, coke sedimentation, or sintering can negatively effect the catalyst. For suitable regeneration processes, one has to bear in mind the exact process conditions as well as the type of catalyst.

Many different methods have been proposed for regeneration of the catalyst, most of them based on application of different gases, such as hydrogen, air, and carbon monoxide.

[0008] US 3,958,957 reports about regeneration of a catalyst through oxidation by air. US 4,151,190 refers to a method for regenerating a catalyst by hydrogen gas at 500 to 600°C, applying a process that takes 16 hours of time. The catalyst used according to US 4,738,948 contains Co and Ru and was regenerated by hydrogen gas at temperatures between 150 to 300 °C. US 5,728,918 describes a method for regenerating a cobalt based catalyst comprising a support, which is used to synthesize C_5^+ hydrocarbons. This method includes the application of carbon monoxide and 30 percent of hydrogen gas at a temperature which is 10°C higher than the one usually used during FT process (that is 220 to 230 °C), under pressure of from 0.5 to 10 bars for 1 to 15 hours. The cobalt based catalyst used in the FT process described in the US 4,595,703, was regenerated by making use of hydrogen gas in the presence of nitrogen, carbon monoxide and methane gas at the same temperature as the reaction temperature.

[0009] However, all processes described in the prior art suffer from drawbacks, which often appear in connection with the use of hydrogen gas during a catalyst regeneration process, which is expensive. Still further, the process has to be stopped for catalyst regeneration.

[0010] Methods making use of oxygen for catalyst regeneration leads to the drawback that, although the catalyst activity seems to return to its initial value, the iron components are oxidized. This makes it necessary to have another preparation stage that is time consuming and leads to increased costs, as a result of the need to prepare pure oxygen. Still further, such regeneration cannot achieve a reactivation of a Zeolite fraction within a catalyst. That leads to the effect that the octane number of produced gasoline does not return to the initial value after the regeneration stage.

[0011] On the other hand, regeneration by hydrogen is, as mentioned before, very expensive because of the pure hydrogen consumed.

[0012] The regeneration process of a catalyst depends on multiple factors, such as operation conditions of the reactor type, the structure of the catalyst, the type of end products and the reduction and activation conditions for the particular catalyst. As a result, finding a suitable regeneration process differs from case to case, even if with a similar process only operation conditions are changed.

[0013] According to the art, most of the catalysts, based on iron or cobalt, are less complex in their structure. Regeneration includes the elimination of the sediment coke built on the surface of the catalyst by hydrogenation and/or combustion with oxygen. For such regeneration processes, the whole FT process has to be stopped and then resumed after the regeneration step.

[0014] Hence, there exists a strong need for providing a catalyst that is easy to regenerate and thus shows a prolonged life time when used in a FT process. Still further, the regeneration should take place while the FT process is running, i.e. an interruption of the process has to be avoided.

[0015] It has now surprisingly been found that a catalyst based on iron compounds as catalytically active species, comprising further Zeolite components shows superior qualities during FT synthesis processes, in particular as to superior possibilities for its regeneration. Making use of such a catalyst, the whole FT can be run continuously without any interruption for catalyst regeneration. The whole process, including the regeneration process of the catalyst can be furthermore improved with adopting particular process parameter, such as the space velocity, which makes an easy regeneration of the catalyst possible while continuously running the process.

[0016] Without any limitation as to this explanation, it is believed that the modification of catalytic behaviour of Fe catalysts further comprising a Zeolite can be explained by positive influence of the Zeolite during an undesired deactivation process of the catalyst. That is, sedimentation of coke on the catalyst's acidic active sites can be diminished. As a consequence, the Fe catalyst has a longer lifetime. As to the lifetime, the catalyst's lifetime is up to two times longer as compared with conventional catalysts that need to be regenerated according to known processes. A major advantage occurring when making use of the catalyst of the invention during a process also encompassed by the invention is that the regeneration of the catalyst can take place during a running process. There is no more need to stop the process, which leads to a much more economic process as compared to prior art processes.

[0017] Generally, in the case of a bifunctional iron catalyst modified with the Zeolite, as suggested by the present invention, the deactivation of the catalyst is to be regarded in connection with the following parameters:

First of all, sedimentation of carbon compounds on the active sites of the iron - Zeolite catalyst leads to deactivation. The formation of those precipitates is a result of the decomposition of methane and the disproportionation reaction of carbon monoxide (Boudouard reaction), that are shown below:

$$CH_4\ C + 2H_2 \qquad \Delta H^\circ = +\,17.9 kcal\,/_{mol.\ Cs}$$

$$2C0\ CO_2 + C \qquad \Delta H^\circ = -41.21\ kCal/_{\mathrm{mol.Cs}}$$

[0018] The decomposition of methane is endothermic while the disproportionation of CO is exothermic. So, by increasing the temperature, the methane decomposition increases, while the disproportionation of CO declines.

[0019] Recent calculations show that under conditions similar to those usually present in a FT process, the major cause of carbon sedimentation is the disproportionation of CO. As a consequence, the control of that reaction is a major task and it should be avoided that temperatures increase to such an extend that the reaction becomes uncontrollable.

[0020] Such high temperatures are to be avoided also from another point of view, namely that sintering of metallic particles also results from unlimited temperatures appearing in the system.

[0021] Another aspect when regarding the activity of a catalyst in a FT process is the coverage of the Zeolite components present in the system, as a result of which the active acidic sites are hidden from the reactants and don't take part in the overall reaction.

[0022] While high temperatures and hence the presence of carbon, which compound deactivates the catalyst, lead to a significant decrease in conversion of the feed stream, coverage of active acidic sites of the catalyst leads to reduced conversion of olefins to aromatic compounds, i.e. the selectivity towards the aromatic compounds is decreased.

[0023] According to the present invention, the advantageous catalyst and a process for its regeneration lead to significant and up to two times longer life times of the Fe Zeolite catalyst while the whole FT process runs without interruption and with a constant selectivity of the catalyst throughput.

[0024] The following examples are suited to illustrate the invention in further detail without restricting its scope:

Example 1

Preparation of the catalyst:

[0025] The Fe catalyst is prepared by the co- precipitation of a solution of respective cations Fe^{2+}, Fe^{3+} and Cu^{2+} with a bicarbonate or sodium carbonate solution.

[0026] The solutions of the cations are prepared by completely dissolving 0.035 to 0.095 mole (of copper nitrate, 0.1 to 0.8 mole of Fe (III) chloride, a solution of 0.6 to 1.5 mole of Fe (II) chloride per litre of water, in such a way that the total amount of cations per litre of the solution is not less that 0.4 mole, and more than 0.6 mole. The solutions of the cations were prepared in amounts of between 2 to 10 and preferably of between 4 to 6 litres. The precipitating solution is prepared by dissolving sodium bicarbonate or sodium carbonate in an amount of 200 to 400 grams, equivalent to the solutions of the cations, in deionised water. Both solutions are heated up to 60 to 80 °C, and are then added to the precipitation system that contains 100 to 1000 millilitres of deionised water, that is heated up to the same temperature used for the ionic solutions. The rate of the addition of the solutions to the precipitation system is controlled such that the pH value of the solution remains between 5 to9. The precipitates are filtrated off and washed with deionised water for several times to eliminate all the remaining cations and anions. In order to add the alkaline salt and surface area modifiers (, potassium silicate together with a silica-sol solution is added to the resulting cake. For the addition of the before mentioned solutions the amount of potassium oxide has to be between 1 to 3 percent by weight and that the percentage of silicon dioxide should not exceed 15 to 25 percents by weight, based on the amount of iron present. The resulting catalyst is dried at a temperature of from 100 to 150 °C for 12 to 30 minutes and is calcinated at 400 to 500 °C in an air flow, for 4 to 8 hours. The atomic ratio of iron of the resulting catalyst is calculated based on the formula a [M/(M+Fe)] x 100 (where M represents all metal oxides). The atomic ratios of the resulting iron catalyst is as follows:

$$100Fe/3\text{-}10Cu0/0.5\text{-}3K_2O/15\text{-}25\ \mathrm{SiO_2}$$

[0027] In a further step, the Zeolite is mixed with the iron catalyst: the Zeolite part of the catalyst is an HZSM5 with a silica to alumina ratio between 12 to 40. The proposed catalyst is composed of a physical mixture of the iron catalyst with the Zeolithe, prepared from the mentioned Zeolite with using a molecular sieve having a mesh of 100 to 150, to homogenize the size.

[0028] The weight percent of the final Fe- Zeolite catalyst is composed of from 10 to 30 percent of iron and from 70 to 90 percent of the Zeolite.

[0029] For the formation of the final catalyst an appropriate adhesive agent having a good thermal and mechanical as well as abrasion resistance is formed, which adhesive agent does not have any negative effect on the selectivity of the desired end products and the activity of the catalyst. Alumina, silica and silica - alumina gels were used for this purpose, in total weight percents of from 10 to 30. The alumina gel was prepared by dissolving respective aluminium salts in deionised water and precipitating them with ammonium salts.

[0030] The silica gel was prepared by precipitating a silica sol solution with nitric acid, and a alumina-silica gel was produced by dissolving aluminium salts in a silica sol solution and precipitation by adjusting the pH at values of between 5 to 9.

Example 2:

Preparation of the iron catalyst

[0031] The iron catalyst was prepared from aqueous salt solution of contain Fe2+, Fe3+ and Cu2+ with sodium carbonate solution, using the co-precipitation method.

[0032] The mixture of cations was prepared by dissolving exactly 0.035 to 0.095 mole of copper nitrate, 0.60 to 1.50 mole of iron (III) chloride and 0.10 to 0.80 mole of iron (II) chloride in one liter of total solution. The precipitating solution was prepared by dissolving sodium bicarbonate or carbonate in an amount of 200 to 400 grams, in a volume of deionized water, equivalent to those of the cation solutions. Bath solution were heated up to 60 to 80 °C and added to a precipitation system containing 100 to 1000 ml of equivalently heated deionized water. The addition rate was adjusted in a way that the pH of the solution remained in the range of 4 to 10. The precipitates were filtered and washed thoroughly with deionized water for several times in order to remove the excess cations and anions. A suitable amount of potassium silicate and silica sol was added to the formed cake, in a way that the amount of potassium and silicon oxides do not exceed 1 to 3 and 15 to 25 percents by weight respectively. The formed catalyst was heated in 100 to 150 °C for 12 to 30 hours and was calcinated in 400 to 500 °C in an air flow for 4 to 8 hours. The atomic ratio of the formed catalyst with respect to iron was calculated using the [M/(M+Fe)] x 100 formulas where M represents metal oxide the atomic ratios for the prepared catalyst are:

$$100\ \mathrm{Fe}/3\text{-}10\ \mathrm{CuO}/0.5 - 3\ \mathrm{K_2O}\ /\ 15\text{-}25\ \mathrm{SiO_2}$$

Mixing the Zeolite with the iron catalyst

[0033] An HZSM5 catalyst with a silicon to Alumina ratio of 12-40 was prepared, using the method disclosed in the Iranian patent No. 25 845. The catalyst according to the invention was prepared by physically mixing the prepared iron catalyst with HZSM5 Zeolite. A sieve with mesh size of 100 to 150 was used for adjusting the size. The catalyst was prepared in such a way that the eight percent of iron were present and between 10 to 30 and 70 to 90 weight percents of the catalyst are zeolite.

Forming the final catalyst

[0034] For the catalyst of the present invention, a suitable binder is one of the important features. The silica gel was prepared by precipitation of silica sol by nitric acid and the silica-alumina gel was prepared by dissolving aluminium salts in a silica sol and then precipitation by controlled pH in a range of 6 to 8.

Comparative Example 3

[0035] FT process making use of known catalysts and their regeneration during the process.

[0036] During the process, there are various methods useful for regeneration of the catalyst. For example, there exists an oxidation and reduction method. As to the oxidation method, oxygen or air is used for burning hydrocarbons or coke remaining in or onto the catalyst. For the reduction method, the heavy hydrocarbons remaining on the catalyst as well as the coke placed on the active sites of the catalyst are converted to methane in a process called methanation making use of hydrogen.

[0037] According to these two methods, after deactivation of the catalyst the reaction is stopped to perform the regeneration.

Example 4

[0038] FT process making use of a catalyst according to the invention and its regeneration during the process

[0039] When using the before described iron catalysts in accordance with the invention in the FT process, a water - gas shift reaction is observed in addition to the main process, which is caused by the absorption of carbon monoxide on the catalyst surface, the formation of surface carbides and chain growth. A water - gas shift reaction includes the reaction of carbon monoxide with water and the formation of carbon dioxide and hydrogen. This reaction is shown below:

$$CO + H_2 O\ C0_2 + H_2$$

[0040] As apparent form the above equation, hydrogen gas is produced during the water - gas shift reaction. This produced hydrogen can be used to regenerate the catalyst. In a process according to the invention, the occurrence of the water-gas shift reaction among the total reactions is increased. Such an effect can be achieved by decreasing the space rate of the feed to 20 to 70 percents (based on the total volume of the reaction) and hence 90-99 percents of carbon monoxide is converted to hydrogen through the water-gas shift reaction. This provides enough hydrogen to regenerate the catalyst. The process to regenerate the catalyst by the produced hydrogen is performed at temperatures of the catalyst bed of between 280 to 300°C and under a pressure of 10 to 30 bars, after every 120 to 200 hours of the running process. The iron catalysts according to the invention can successfully be regenerated by such a process without any need to stop the process, i.e. the regeneration process can be achieved with simultaneously running the main process.

Example 5

[0041] The Fe-Cu - k catalyst was prepared by coprecipitation of iron and copper salts (Iron nitrates and copper nitrates), under controlled pH and temperature, with a final addition of potassium oxide. The prepared Fe catalyst was then physically mixed with the commercial HZSM5 Zeolite () by addition of silica - alumina gel (with a ratio of 70 to 10 percents of silica, and 30 to 90 percents of alumina) as an adhesive agent (in an amount of 10 to 15 weight%). The catalyst was formed to cylindrical pills with a diameter of about 4 mm and a length of 3 mm making use of a tableting press. The final catalyst was calcinated in airflow, at 450 °C.

[0042] The activity of the catalyst was tested in a fixed-bed steel reactor of 2cm in diameter, which was furnished with a thermowall and a thermo couple.

[0043] The flow of feed is controlled by mass - flow meters. The heating system consists of electrical heating jackets, each of which is controlled by a temperature controller. The temperature of the reactor outlet that passes through a pressurized container to collect the yielded liquid is lowered with a cooling system. The catalyst was moved to a reactor and finally prepared by reduction and carbonization stages. In the reduction stage, the catalyst stayed in a flow of nitrogen containing 5 to 8 percents by volume of hydrogen with a space rate of from 10 to 20 liters (g.Fe.h)$^{-1}$ and was heated up to 250-270°C, with a temperature gradient of 10 °C /min.

[0044] The carbonization stage was performed with a 1:1 carbon monoxide and hydrogen flow, having a space rate of from 1-4 nl (g.Fe.h)$^{-1}$ under atmospheric pressure for 24 hours. Then the support temperature of the catalyst was increased up to 280 to 300°C while at the same time the pressure was increased up to 10 to 30 bars, while a flow with a 0.5 to 2 carbon monoxide to hydrogen ratio passed through the system with a space rate of 2 to 4 liters (nl="normal liters) (g.Fe.h)$^{-1}$. The regeneration by reduction of feed rate process was quickly performed, while the reaction was in process, after every 120 to 200 hours. During each regeneration reaction, the space velocity of the feed was reduced to 20, 45 and 70 percents of its initial values. As mentioned before, the initial values are 2 to 4 liters $(g.Fe.h)^{-1}$.

[0045] The reaction was performed for 641 successive hours, during which the octane number of the product remained constant at about 95. Running the process under such conditions did not only prevent the catalyst from deactivation but also the capacity of the catalyst was increased, resulting in better conversion rates, becoming even better after each recycling step.

[0046] The following table shows data of the product stream after different reaction times

Time on Stream (h)	112	353		641
The reactor outlet analysis (w%)				
H_2	3.11	2.6		2.33
CO	40.39	34.70		18.08
CO_2	32.46	36.08	49.57	
H_20	7.23	6.72		6.77
*HC	16.81	19.90	23.25	
**	95.92	95.73	94.47	
C.R.O.N				

*Hydrocarbon

**Calculated research Octane Number

Claims

1. Bifunctional iron catalyst for use during a single-stage gasoline production process from syngas, which catalyst comprises

    a) iron oxide
    b) optionally further metal oxides
    c) a zeolith and
    d) a binder.

2. Catalyst according to claim 1, wherein the binder is a silica-alumina gel.

3. Catalyst according to claim 1 and/or 2, wherein the zeolith is a zeolite with a silica to alumina ratio of 12 to 40.

4. Catalyst according to any of the preceding claims, wherein the zeolith has a pore size of more than 5 A°.

5. Catalyst according to any of the preceding claims, wherein the zeolith is H-ZSM5.

6. Catalyst according to any of the preceding claims, wherein 70 to 90 percent of H-ZSM5 are used.

7. Catalyst according to any of the preceding claims, wherein the catalyst further comprises copper and/or potassium and/or silicon oxides.

8. Catalyst according to claim 7, wherein the amounts of copper oxide ranges from 3 to 10 percents by weight.

9. Catalyst according to claim 7, wherein the amounts of potassium oxide ranges from 15 to 25 percents by weight.

10. Catalyst according to claim 7, wherein the amounts of silicon oxide ranges from 0.5 to 3 percents by weight.

11. Catalyst according to any of the preceding claims wherein the catalyst is in the form of cylindrical pellets having a diameter of from 3 to 6 mm and a height of from 3 to 7 mm.

12. A gasoline production process from syngas making use of a catalyst as claimed according to claim 1.

13. The process according to claim 12, where in the catalyst is recycled while the process is still running.

14. The process according to claim 11 and/or 12, wherein the regeneration of the catalyst is achieved by decreasing the feed space velocity in a certain period.

15. The process according to claim 14, wherein the space velocity of the feed is decreased by up to 20 to 70 percents of the initial rate. this initial rate is 2 to 4 liters (g.Fe.h)$^{-1}$

16. The process according to one or more of claims 13 to 15, wherein the system's temperature during the regeneration process is between 280 to 300°C.

17. The process according to one or more of claims 13 to 16, wherein the system pressure during the regeneration process is between 10 to 30 bars.

18. The process according to one or more of claims 13 to 17, wherein the regeneration process is repeated after 120 to 300 working hours by reducing the space velocity of the feed.

19. The process according to one or more of claims 13 to 18, wherein more than 90 % of the carbon monoxide are converted to hydrogen during a water-gas shift reaction.

20. The process according to one or more of claims 13 to 19, wherein the lifetime of the catalyst is significantly prolonged when compared with the lifetime in a process making use of conventional catalyst regeneration processes.

European Patent Office

EUROPEAN SEARCH REPORT

Application Number
EP 04 10 5668

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.7)
X	US 4 622 308 A (KOIKEDA ET AL) 11 November 1986 (1986-11-11) * column 3, line 58 - line 68 * * column 7, line 19 - column 8, line 2; claim 1 * -----	1-7,11, 12	C10G2/00 C07C1/04
X	EP 0 148 048 A (COMPAGNIE FRANCAISE DE RAFFINAGE SOCIETE ANONYME DITE:) 10 July 1985 (1985-07-10) * page 1, line 4 - line 11 * * page 4, line 15 - line 25 * * page 6, line 11 - line 13; claims 1,2,5,7,8; example 3 * -----	1-12	
X Y	US 4 207 208 A (BRENNAN, JAMES A ET AL) 10 June 1980 (1980-06-10) * column 3, line 45 - line 62 * * column 6, line 7 - line 8; claim 1; example 2 * -----	1-5,11, 12 13-20	
Y	US 2 540 109 A (FRIEDMAN ALVIN H) 6 February 1951 (1951-02-06) * column 1 - column 2; claim 1 * -----	13-17, 19,20	**TECHNICAL FIELDS SEARCHED (Int.Cl.7)** C10G C07C
Y	US 6 022 755 A (KINNARI ET AL) 8 February 2000 (2000-02-08) * column 1, line 33 - column 2, line 55; claims 1,4,5; examples 1,2 * -----	13,14, 17-20	

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
The Hague	22 March 2005	Deurinck, P

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
Y : particularly relevant if combined with another document of the same category
A : technological background
O : non-written disclosure
P : intermediate document

T : theory or principle underlying the invention
E : earlier patent document, but published on, or after the filing date
D : document cited in the application
L : document cited for other reasons
&: member of the same patent family, corresponding document

1

ANNEX TO THE EUROPEAN SEARCH REPORT ON EUROPEAN PATENT APPLICATION NO.

EP 04 10 5668

This annex lists the patent family members relating to the patent documents cited in the above-mentioned European search report.
The members are as contained in the European Patent Office EDP file on
The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

22-03-2005

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 4622308 A	11-11-1986	JP 1586729 C	19-11-1990
		JP 2008776 B	27-02-1990
		JP 57190083 A	22-11-1982
		JP 58052387 A	28-03-1983
		AU 550415 B2	20-03-1986
		AU 8361882 A	25-11-1982
		CA 1176228 A1	16-10-1984
		DE 3218787 A1	02-12-1982
		GB 2099716 A ,B	15-12-1982
EP 0148048 A	10-07-1985	FR 2556237 A1	14-06-1985
		AU 3637784 A	12-06-1986
		EP 0148048 A1	10-07-1985
		JP 60139342 A	24-07-1985
		ZA 8409560 A	31-07-1985
US 4207208 A	10-06-1980	NONE	
US 2540109 A	06-02-1951	NONE	
US 6022755 A	08-02-2000	GB 2299767 A	16-10-1996
		AU 5348896 A	23-10-1996
		NO 974606 A	06-10-1997
		WO 9631276 A1	10-10-1996

EPO FORM P0459

For more details about this annex : see Official Journal of the European Patent Office, No. 12/82