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(21) International Application Number: PCT/AU89/00173 (22) International Filing Date: 20 April 1989 (20.04.89) (30) Priority data: PI 7940 28 April 1988 (28.04.88) AU (71)(72) Applicant and Inventor: SEDDON, Duncan [GB/AU]; 116 Koornalla Crescent, Mount Eliza, VIC 3930 (AU). (74) Agent: GRIFFITH HACK & CO.; 601 St. Kilda Road, Melbourne, VIC 3004 (AU). (81) Designated States: AT (European patent), AU, BE (European patent), CH (European patent), DE, DE (European patent), FR (European patent), GB, GB (European patent), IT (European patent), JP, LU (European patent), NL, NL (European patent), NO, SE (European patent), SU,		US. Published <i>With international search report.</i> <i>With amended claims.</i>	
(54) Title: CATALYSTS FOR OLEFIN AND PARAFFIN CONVERSION			
(57) Abstract A catalyst for converting paraffins, olefins or mixtures of both into a hydrocarbon product rich in aromatics and a gas of high energy content. The catalyst comprises a crystalline gallium-silicate of the ZSM-5 family and is prepared from a gallo-silicate gel. The gel has a silica to gallia mole ratio lying in the range between 80 and 115 and a silica to alumina mole ratio greater than 100. The gas of high energy content is a gaseous hydrocarbon having a high energy content per unit volume.			

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TITLE: CATALYSTS FOR OLEFIN AND PARAFFIN CONVERSION**BACKGROUND**

Simple aromatic molecules such as benzene, toluene and xylene are key components and building blocks in many facets of modern industrialised societies. They find use as building blocks and intermediates in synthetic fibre manufacture such as polyesters and nylon, and intermediates in bulk commodity plastics such as polystyrene. They also find use as components of special hydrocarbon solvents. The supply of these aromatic molecules to modern industry is thus of crucial importance.

Recently, with the widespread wish to control air pollution, small aromatic molecules, particularly toluene and xylene, have found an

increased role as octane boosters in unleaded gasoline. This increased demand for the smaller aromatic molecules increased their value relative to other hydrocarbon molecules.

By contrast, paraffinic molecules, especially linear molecules, being low in octane, have become less favoured as gasoline components. Paraffins are available from a wide range of sources. For example, in the recovery of natural-gas large quantities of paraffins, usually known as condensate, and paraffinic gases, referred to as LPG, are often co-produced with the gas. Paraffins, together with small olefins are also produced in large quantities from refinery operations such as catalytic cracking and hydrocracking.

By far the largest source of paraffinic material is in the naphtha fraction of crude oil. For many decades the petroleum refining industry has used this liquid fraction as a source of aromatics in the process known as catalytic reforming. Catalytic reforming is a large scale operation using expensive platinum based catalysts and requiring large high pressure plants. Most reforming processes are unsuitable for turning either the lighter paraffins or LPG into aromatics.

It has been recently shown that the smallest paraffin, methane (which is the largest component of natural-gas), can be oxidatively coupled to ethylene, the smallest olefin. Ethylene can be converted into transport fuels using acidic zeolite catalysts. This opens the way for the mass conversion of natural-gas into fuels.

The purpose of the present invention is to produce small aromatic molecules from paraffins, boiling from ethane upwards, and olefins from ethylene upwards, using catalysts and process plants which are cheaper than catalytic reforming.

SUMMARY OF THE INVENTION

The invention concerns the conversion of paraffins and olefins into aromatics by zeolite catalysts. The conversion of paraffins and olefins into aromatics has been described in Australian Patent 509285 (to British Petroleum plc), this patent describes the preparation and use of gallium impregnated and ion-exchanged ZSM-5 zeolite catalysts. Australian Patents 479875 and 484974 (both to Mobil Oil Corp.) describe the use of zinc exchanged zeolite to effect paraffin conversion into an aromatic rich product.

The above processes utilise a conventionally synthesised ZSM-5 zeolite which is subsequently impregnated or exchanged with the promoting metal either gallium or zinc. The conventionally synthesised ZSM-5 zeolite contains aluminium in the crystal lattice.

Zeolites with gallium in the lattice have been known for a long time (see "Zeolite Molecular Sieves" by D.W.Breck published in 1974).

Zeolite catalysts with gallium in the lattice have been described in Australian Patent 558232 (to Shell International Research Maatschappij B.V.) This patent describes gallium compositions made from gels with a silica/gallia mole ratio of 25-100. As well as aromatic rich liquids these catalysts gave a high selectivity to hydrogen gas. Such byproduct hydrogen is useful in developed centres where there is a growing demand for molecular hydrogen. However, if the hydrogen gas is useless at the place of aromatics production, then its presence in the byproduct gases lowers the energy content (in volume terms) of the byproduct which makes it less useful as a fuel and places a constraint on selling the byproduct to other users.

We have discovered that an improved catalyst can be made from a zeolite synthesised from a silicate gel containing a source of gallium and containing substantially no aluminium. After crystallisation of the gel and the transformation of the zeolite into the acid form, the said zeolite can be beneficially used for the conversion of paraffins and olefins from ethane and ethylene upwards into aromatics or aromatic rich blendstock and a high energy content (in volume terms) hydrocarbon gas, without further ion-exchange or impregnation with gallium or zinc. The said silicate gel preferably has a silica/gallia mole ratio >10 , and silica/alumina mole ratio >100 , the alumina coming from common impurities in the starting materials. The conversion of the paraffins and olefins occurs at temperatures preferably from 300°C upwards, and at low pressure in the absence of added hydrogen.

DESCRIPTION AND PREFERRED EMBODIMENTS

Zeolite catalysts are a crucial feature of the invention. Zeolites and zeolite like materials are described in "Zeolite Molecular Sieves" by D.W.Breck published in 1974. Of particular interest are zeolites of the ZSM-5 family some of which are described in Australian Patents 424568, 446123, 450820 and 458708 (all to Mobil Oil Corp.).

The zeolites of the invention are characterised by an open pored structure which will allow the entry of paraffinic molecules, and more importantly the egress of the small aromatic molecules of interest. The zeolite structures of interest can be characterised by vacuum microbalance sorption using simply branched paraffins such as 3-methylpentane as sorbent. The zeolites of interest will, in the hydrogen or acid form of the zeolite, sorb more than 2% by weight of the sorbent at a pressure of 2kPa. Another way to judge the suitability

of the structure will be from crystallographic evidence, where if the zeolite possesses pores greater than about 5Å in size then the zeolite structure would be suitable.

Zeolites are usually regarded as crystalline alumino-silicates although it is now recognised that combinations of many other elements can give open pore structures similar to the alumino-silicate zeolites. A distinguishing feature of the zeolite materials of this invention is that they are formed in a gallo-silicate form, i.e. gallium is substituted for aluminium in the synthesis of the zeolite and the zeolite structure is essentially free of aluminium. It will be recognised that aluminium is a common impurity in gallium and silica source materials and small quantities of aluminium may be present. Thus the zeolite catalysts of the invention will have a silica/alumina mole ratio of at least 100.

A particular feature of the gallo-silicates of the invention is that gallium is added at the time of synthesis. Methods of adding gallium include as oxide or as a soluble salt such as gallium nitrate, which is added to the synthesis gel before the zeolite is crystallised. The preference is for a silica/gallia mole ratio of at least 10, although lower ratios may be used.

Another feature of the zeolites of the invention is that the zeolite will be capable of being transformed into a solid Bronsted acid. The method by which this is achieved is dependent upon the particular zeolite used. Many methods are described in the literature. Some zeolites are incapable of being transformed and structure collapse will occur reducing the zeolites ability to sorb pertinent simply branched paraffins.

In order to be useful, the zeolite will be fabricated into a solid particle, chip or pellet. This fabrication may or may not require the assistance of a binder or inert diluent material. The choice of binder and size of particle will be determined by the engineering requirements of the equipment in which the catalyst is to be used. For a fixed bed reactor, tablets of 5mm or more in diameter may be the choice. For a fluid bed reactor a smaller 30–100 μ m particle of high attrition resistance may be the choice. Such fabricated catalysts may necessitate the mixing of the zeolite with diluents such as alumina or clays, e.g. bentonite. In some instances the binder may not be totally inert but may provide a co-catalytic role by, for example, bringing additional acid sites or dehydrogenation function to the final catalyst composite.

The catalyst of the invention is used to convert paraffinic or olefinic hydrocarbons by contact with the feedstock in the gaseous phase. The paraffinic feedstock may range from LPG to heavy naphthas, be individual components such as propane, or wide ranging mixtures. Present with the paraffin may be naphthenic materials, *cyclo*-paraffins, olefins such as ethylene or propylene or aromatics. The paraffins may be branched or linear or any mixture. The feedstock may be very rich in olefins. In a likewise manner the olefin feedstock may be very rich in paraffins, be linear or branched or any mixture, or contain aromatics.

The olefins of interest may be ethylene, produced by pyrolysis of higher hydrocarbons else as the product of oxidative coupling of methane or the high temperature catalytic pyrolysis of methane. Olefins such as propylene are produced as byproduct in the catalytic cracking of hydrocarbons. In these instances the olefin feed will contain significant quantities of paraffin from methane onwards in molecular weight.

The conversion conditions used will depend upon the nature of the feedstock. At one extreme are products from oxidative coupling of methane in which ethylene and ethane might be diluted with a large excess of methane. The efficient conversion of the paraffins and olefins in such a feedstock might be best brought about at high temperatures e.g. 600–700°C and relatively low space velocity e.g. 0.1hr⁻¹. For the most part however conversion conditions will be much less severe. For a more typical feed of C₃ and higher paraffinic hydrocarbons, conversion is brought about by contacting the feedstock at a temperature from 350 to 600°C, preferably 400 to 550°C and at a weight hourly space velocity ranging from 0.1 to 20hr⁻¹, preferably 0.5 to 5hr⁻¹. For a feedstock comprising substantially olefins, conversion can be brought about at lower temperature e.g. 300°C.

No limits are placed on the pressure of the process but a particular advantage is that the conversion can be performed at a relatively low pressure, that is about 100 to 1000kPa hence avoiding the requirements of high pressure equipment.

A distinguishing feature of the catalysts and the process of the invention is that no additional hydrogen need be added to the feedstock; this contrasts with catalytic reforming which is usually conducted in the presence of a substantial hydrogen partial pressure.

Another distinguishing feature is the energy content, in volume terms, of the byproduct gas.

When paraffins such as butane are converted into aromatics over catalysts of the invention, then the main light byproducts are hydrogen, methane, ethane, ethylene, propane and propylene. After separation of the liquid product some of these light gaseous products may be

recycled so as to increase the overall yield of aromatics (principally by converting all of the olefins and more of the propane). However, methane and ethane would not be converted and would have to be purged from the system together with some residual olefin and propane. For use as a fuel (either within the plant or exported to another user), it is important to maximise the energy content, in volume terms, of these purged gases. Using butane or a higher homologue, the catalyst of the invention will give a light gaseous byproduct, containing methane, ethane and propane, with an energy content greater than 900BTU/ft³. Starting from propane, the catalyst of the invention will give a light gaseous product, containing methane and ethane, with an energy content greater than 800BTU/ft³.

Many modifications to the preferred embodiments and examples may be made without departing from the spirit and scope of the invention.

The invention is further illustrated by the following examples.

EXAMPLE 1

This example illustrates the synthesis of the zeolite of the invention.

A gel was made up by mixing together sodium hydroxide (7.4g) dissolved in water (50.0g), a dispersion of silica (made from Cab-O-SilTM (133.4g), water (800g) and gallium nitrate solution (230ml, 0.179M)), and a solution of tetra-n-propylammonium bromide (73.9g) in water (200g). After mixing, sodium chloride (250g) was stirred in. The pH of the gel was adjusted to 11.3 by the addition of a further portion of sodium hydroxide solution (45ml of 10% wt/wt). The zeolite gel had a silica/gallia mole ratio of 107. The zeolite was crystallised in a stirred autoclave at 170°C over 16hr. The as-made

product was transformed to the acid form by ion-exchange with ammonium nitrate solution, followed by calcination to 500°C. The ion-exchange and the calcination steps were repeated.

The product zeolite was shown to be of the ZSM-5 structure by powder x-ray diffraction. Vacuum microbalance studies gave 11.4% n-hexane and 7.6% 3-methylpentane sorption at 2kPa.

Before use the zeolite was fabricated into 3mm tablets using CatapelTM, a pseudo-boehmite alumina phase, as binder, (1:4 wt/wt).

EXAMPLE 2

This example illustrates the use of a catalyst prepared in the above manner.

The catalyst (10g) was charged to a stainless steel reactor of conventional downflow geometry. Liquid feedstock was vapourised in a preheater and aromatic rich product collected using a condenser placed immediately after the reactor, before use the catalyst was dried on a stream of nitrogen for 3hr at 400°C. The following results were obtained at 500°C and a WHSV of 1hr^{-1} . Analysis was performed by gas-chromatography. Because of the small scale of this test these results merely illustrate the types of feedstock that can be processed.

TABLE 1

Feedstock	Propane	Butane	Light Naphtha	Propene	Butene
Product					
Hydrogen	1.3	1.7	2.2	3.5	2.7
Methane	0.9	12.9	5.6	1.0	1.3
Ethylene	2.8	4.4	3.6	3.1	1.2
Ethane	1.1	4.6	3.5	0.6	0.8
Propylene	4.6	3.9	5.0	13.6	2.6
Propane	80.0	13.1	9.1	5.7	6.8
Butanes	1.1	27.7	18.2	4.7	14.7
C ₅ +		2.3	20.4	2.5	5.3
Benzene	3.5	7.8	4.7	13.2	5.8
Toluene	3.4	10.4	11.5	25.1	22.3
Xylene	1.4	6.0	11.6	18.3	21.6
C ₉ + Aromatics		5.3	4.8	8.8	15.0

The above results show that the catalyst of the invention is capable of converting a wide range of paraffinic feedstock, from propane upwards into aromatics. The conversion of olefins such as propene and butenes into aromatic rich products is also illustrated.

EXAMPLE 3

This example compares the catalyst of the invention with the prior-art catalyst prepared in accordance with Australian Patent 509285 by impregnation of a ZSM-5 zeolite with a silica/alumina ratio of 70

with gallium nitrate solution. The samples were obtained by the incipient wetness using 1M gallium nitrate - alternative-1 - and 2M gallium nitrate - alternative-2. The equipment used was as in Example 2. n-Pentane was fed over the catalysts at 500°C, a WHSV of 1hr^{-1} and at 1 atm. pressure.

TABLE 2

	Selectivity to Aromatics
Catalyst of Example 1	39%
Alternative - 1	28%
Alternative - 2	26%

Selectivity to Aromatics = (Aromatics/Converted Feed) x 100

The example shows the higher concentration of aromatics that can be obtained using the catalyst of the invention.

EXAMPLES 4-8

These examples illustrate the conversion of light hydrocarbon gasses such as mixed butanes or propane can be converted into aromatics using the catalyst of the invention. Conversion was in a fixed bed reactor charged with 1.5kg of catalyst made as in Example 1. The results of the tests are shown in Table 3.

TABLE 3

<i>Feed</i>	EX 4	EX 5	EX 6	EX 7	EX 8
Propane (%)	2.1	0.4	1.7	0.0	92.0
iso-Butane (%)	21.1	14.0	19.7	20.3	0.0
n-Butane (%)	58.8	56.8	59.9	59.9	0.0
Pentanes (%)	18.4	29.7	18.7	19.9	0.0
Temperature (°C)	550	550	500	500	600
WHSV (hr ⁻¹)	1.1	1.0	1.0	1.1	1.0
<i>Products</i>					
C ₄ Conversion (%)	63	70	49	55	37 ^a
Hydrogen(%)	3.8	3.6	3.9	2.2	4.1
C ₁ -C ₃ (%)	48.9	46.2	46.5	57.5	24.6 ^b
Byproduct gas BTU/ft ³ .	958	954	943	1343	815
Selectivity to Aromatics (%)	47.5	50.7	46.3	40.0	60.8

(a) propane conversion (b) methane and ethane

EXAMPLES 9-12

These examples illustrate the conversion of light paraffinic liquids such as mixed pentanes are easily converted into aromatics using the catalyst of the invention. Conversion was in a fixed bed reactor charged with 1.5kg of catalyst made as in Example 1. The results of the tests are shown in Table 4.

TABLE 4

<i>Feed</i>	EX 9	EX 10	EX 11	EX 12
iso - Pentane (%)	47	47	47	47
n - Pentane (%)	44	44	44	44
Hexanes + (%)	7	7	7	7
Temperature (°C)	500	600	550	475
WHSV (hr ⁻¹)	1.0	1.9	2.2	1.9
<i>Products</i>				
C ₅ Conversion (%)	93	87	82	74
Hydrogen	1.8	1.9	2.2	1.9
C ₁ - C ₃ (%)	33.5	53.1	45.9	20.4
Byproduct gas ^a BTU/ft ³ .	1164	1032	1007	1007
Aromatics (%)	46	26	27	29

(a) contains butanes

EXAMPLE 13

This example illustrates the conversion of a light naphtha derived from natural gas into an aromatic rich stock using the catalyst of the invention. Conversion was in a fixed bed reactor charged with 1.5kg of catalyst made as in Example 1. The results of the tests are shown in Table 5.

TABLE 5

<i>Feedstock</i>	n-butane	4.86%	isoheptane	7.79%	n-nonane	8.21%
	isopentane	4.49%	n-heptane	10.74%	isodecane	2.59%
	n-pentane	8.06%	isooctane	8.62%	n-decane	6.97%
	isohexane	6.89%	n-octane	9.8%	undecane	4.2%
	n-hexane	10.02%	isononane	5.27%	dodecane +	1.43%
Temperature (°C)		475	550	550		
WHSV (hr ⁻¹)		0.9	1.8	1.0		
% BTX in Liquid Product		73.5	75.5	79.0		
% Gas		52.5	60.2	61.1		
Byproduct gas BTU/ft ³ .		1340	1466	1381		

EXAMPLES 14-16

These examples illustrate the conversion of ethylene into aromatics using catalysts of the invention. Two catalysts were prepared as described in Example 1 (Examples 14 and 15). Another catalyst based on conventional ZSM-5 with silica/alumina ratio of 71 was used for comparative purposes (Example 16). Conversion was in a conventional downflow reactor using 50g of catalyst which, in order to control the high exotherm of ethylene conversion, was further diluted with 50g of inerts (DenstoneTM Balls). Results of the tests are given in Table 6.

Although conversion and liquid yields are similar, the results show that the catalysts of the invention increases the aromatic content of the liquid gasoline produced.

TABLE 6

	EX 14	EX 15	EX 16
Temperature (°C)	513	510	500
WHSV (hr ⁻¹)	1.48	1.52	1.50
Ethylene Conversion (%)	95.0	97.5	97.1
Liquid Yield (%)	48.9	56.3	50.9
% Gasoline	92.0	88.6	91.9
% C ₇₊ Aromatics	51.8	70.0	40.9

THE CLAIMS DEFINING THE INVENTION ARE AS FOLLOWS:

1. A catalyst for converting paraffins, olefins or a mixture of both into a hydrocarbon product rich in aromatics and a high energy content (per unit volume) gas, said catalyst comprising a crystalline gallium-silicate of the ZSM-5 family, prepared from a gallo-silicate gel having a silica to gallia mole ratio between 80 and 115 silica to alumina mole ratio greater than 100.
2. A catalyst according to claim 1 wherein the ratio of silica to gallia lies between 100 and 115.
3. A catalyst according to claim 1 wherein the ratio of silica to gallia is 107.
4. A catalyst according to any of claims 1-3 wherein the paraffin is propane, a higher homologue or mixture thereof.
5. A catalyst according to any of claims 1-3 wherein the paraffin is butane, a higher homologue or mixture thereof.
6. A catalyst according to any of claims 1-3 wherein the olefin is ethylene, a higher homologue or mixture thereof.
7. A catalyst according to any of claims 1-6 wherein the hydrocarbon product is rich in benzene, toluene or xylenes or mixtures thereof.
8. A catalyst according to any of claims 1-5 wherein the gas of high energy content has an energy content greater than 800BTU/ft³.
9. A catalyst according to any of claims 1-3 and 5 wherein the gas of high energy content has an energy content greater than 900BTU/ft³.

10. A method for converting paraffins, olefins or a mixture of both into a hydrocarbon product rich in aromatics and a high energy content (per unit volume) gas, which method comprises passing said paraffins and/or olefins over the catalyst of any one of the claims 1-9.

AMENDED CLAIMS

[received by the International Bureau
on 12 September 1989 (12.09.89);
original claims 1-7 replaced by amended claims 1-7, claim 9 replaced
by amended claim 8, claims 8 and 10 cancelled (2 pages)]

1. A process for converting paraffins, olefins or a mixture of both into a hydrocarbon product rich in aromatics and a gaseous product having a high energy content, which process comprises contacting a stream of paraffins, olefins or a mixture of both with a catalyst, said catalyst comprising a crystalline gallium-silicate of the ZSM-5 family, prepared from a gallo-silicate gel, wherein the molar ratio of silica to alumina in the gel is at least 100:1 and the molar ratio of silica to gallia is selected to produce a hydrocarbon product containing at least 25% by weight aromatics and a gaseous product having an energy content of at least 800BTU/ft³ (gross), said ratio of silica to gallia lying in the range from 80:1 to 115:1.
2. A process according to claim 1 wherein the catalyst has a ratio of silica to gallia which lies between 100 and 115.
3. A process according to claim 1 wherein the catalyst has a ratio of silica to gallia of 107.
4. A process according to any of claims 1-3 wherein the paraffin is propane, a higher homologue or mixture thereof.
5. A process according to any of claims 1-3 wherein the paraffin is butane, a higher homologue or mixture thereof.
6. A process according to any of claims 1-3 wherein the olefin is ethylene, a higher homologue or mixture thereof.
7. A process according to any of claims 1-6 wherein the hydrocarbon product is rich in benzene, toluene or xylenes or mixtures thereof.

8. A catalyst according to any of claims 1-3 and 5 wherein the gaseous product has an energy content greater than 900BTU/ft³.

INTERNATIONAL SEARCH REPORT

International Application No. **PCT/AU 89/00173**

I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all) 6

According to International Patent Classification (IPC) or to both National Classification and IPC

Int. Cl.⁴ B01J 29/02, 29/04, C01B 33/28, C07C 2/08, 2/84

II. FIELDS SEARCHED

Minimum Documentation Searched 7

Classification System |

Classification Symbols

IPC

B01J 29/02, 29/04

US Cl.

423/326, 423/328, 502/61, 502/71, 585/415

Documentation Searched other than Minimum Documentation
to the Extent that such Documents are Included in the Fields Searched 8

AU : IPC as above

III. DOCUMENTS CONSIDERED TO BE RELEVANT 9

Category*	Citation of Document, ¹¹ with indication, where appropriate, of the relevant passages 12	Relevant to Claim No 13
P,X	EP,A,299392 (RESEARCH ASSOCIATION FOR UTILIZATION OF LIGHT OIL) 18 January 1989 (18.01.89)	1-10
X	EP,A,252742 (MOBIL OIL CORPORATION) 13 January 1988 (13.01.88)	1
X	US,A,4704494 (INUI) 3 November 1987 (03.11.87)	1-10
X	EP,A,230356 (RESEARCH ASSOCIATION FOR UTILIZATION OF LIGHT OIL) 29 July 1987 (29.07.87)	1-10
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X	EP,A,223345 (MOBIL OIL CORPORATION) 27 May 1987 (27.05.87)	1-10
E	AU,A,28311/89 (MOBIL OIL CORP.) 13 July 1989 (13.07.89)	1-10
P,X	(& NO,A,890061, 6 January 1989 (06.01.89))	
(continued....)		

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

"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.

"&" document member of the same patent family

IV. CERTIFICATION

Date of the Actual Completion of the
International Search

30 June 1989 (30.06.89)

Date of Mailing of this International
Search Report

(19/07/89) 19 July 1989

International Searching Authority

Australian Patent Office

Signature of Authorized Officer

A W WINCH

III. DOCUMENTS CONSIDERED TO BE RELEVANT (CONTINUED FROM THE SECOND SHEET)

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EX TO THE INTERNATIONAL SEARCH REPORT ON
INTERNATIONAL APPLICATION NO. PCT/AU 89/00173

This Annex lists the known "A" publication level patent family members relating to the patent documents cited in the above-mentioned international search report. The Australian Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

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