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(54) Title: PRODUCING BLENDSTOCK

(57) Abstract

The specification describes a method for producing gasoline blendstock. A naphtha (3) is produced by contacting synthesis gas (1) with a catalyst (2) comprising cobalt supported on a ZSM-5 type zeolite at a temperature in the range from 220 °C to 280 °C. The naphtha is fractionated (4) to remove butane (5) and hydrocarbons boiling in excess of 174 °C (6). Normal paraffins contained in the fractionated naphtha (7) are isomerised (8) to produce a gasolene blendstock. An isomerisation process disclosed comprises separating the normal paraffins from the iso-paraffins (12) contained in the fractionated naphtha by selectively absorbing the normal paraffins on a zeolite molecular sieve (11), desorbing the normal paraffins with hydrogen (13) and passing the so formed stream of hydrogen and normal paraffins (14) over an acidic, metal-loaded molecular sieve (15).

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PRODUCING BLENDSTOCK

TECHNICAL FIELD

The invention relates to an improved reformulated gasoline blendstock obtained from synthesis gas, and a process for producing this blendstock.

BACKGROUND

The increasing push for the reduction of hazardous air pollutants from exhaust emissions will require the reformulation of current gasoline compositions. The phase down of lead has already had a major effect on gasoline composition with increases in aromatics and iso-paraffins, as well as the introduction of ethers such as MTBE (methyl tertiary butyl ether) to compensate for the octane loss due to lead removal.

However, the 1990 amendments to the US Clean Air Act will result in still tighter emission controls with targets including additional gasoline volatility control, an upper limit on aromatics (benzene in particular), restrictions on undesirable hydrocarbons in the gasoline, as well as a requirement for the addition of oxygenates.

To minimise hydrocarbon emissions at the pump and from automotive exhausts the volatility of the fuel, as measured by Reid Vapour Pressure (RVP) will be lowered to 9 psi (61 kPa). This can primarily be achieved by removing butanes from current formulations.

Benzene is undesirable because of its effect on human health as it is a known carcinogen. So despite its high octane value, it will be limited to less than 1 vol %.

Other aromatics are also undesirable because of the toxicity of the emissions they cause and so will have to be limited to meet the targeted emission reductions. This will probably mean a ceiling of the order of 25% aromatics. Other undesirable hydrocarbons in gasoline are those which cause emissions of ozone-forming volatile organic compounds. Heavy aromatics also fall into this group, as well as olefins, which have a high photochemical reactivity. A high endpoint of the gasoline (which is measured by the T90 ASTM distillation procedure) has also been found to contribute to these emissions, and so will be targeted for reduction in reformulated gasolines.

Also, in order to reduce carbon monoxide emissions, a minimum oxygen content of 2% has been targeted. This will promote complete combustion to carbon dioxide rather than carbon monoxide. This may be achieved by the addition of significant quantities of MTBE (11%) or other ethers such as ETBE (ethyl tertiary butyl ether) or TAME (tertiary amyl methyl ether). These are high octane additives, and would compensate for octane losses due to reduction in aromatics and olefin content.

Methanol and ethanol, although oxygenates of high octane, are not as favourable as additives as the ethers because of their high blending vapour pressures and lack of water tolerance.

The entry of reformulated gasolines to the market will thus have an enormous impact on current refinery operations. The majority of the current gasoline pool is made up from fluid catalytic cracking (FCC) naphthas and reformate. However, the biggest problem for reformulated gasoline production, is that aromatics formation in these processes can not currently be prevented, and thus an efficient way of dealing with an oversupply of aromatics must be found, as they would have to be removed from the product by processes such as distillation and extraction.

Another approach is to use a non-conventional feedstock as a basis of the reformulated gasoline, one which contains little or no aromatics. Economic advantages would also result if this feedstock could be obtained from a cheap and abundant source. We have now identified such a feedstock.

The huge supplies of uncommitted natural gas around the world, mainly in remote locations have been the impetus of much research into the conversion of natural gas into liquid transport fuels over the last decade.

Three main routes for natural gas conversion have been commercialised to date. These are methanol synthesis, the methanol to gasoline process and the Fischer-Tropsch synthesis. The last two routes offer an advantage in that no vehicle modifications or changes to the refuelling structure are required.

The methanol to gasoline process, further described in US Patent 3 894 103 (Mobil Oil Corporation), however, produces a high octane gasoline which obtains its octane rating from a very high level of aromatics. So, once again, it would be unsuitable for use in a reformulated gasoline.

A more suitable reformulated gasoline blendstock could, however, be obtained via the Fischer-Tropsch process. The naphthas produced from this process are generally straight chain, paraffinic and non-aromatic. Depending on the catalyst composition used and the operating conditions selected, variations in the characteristics of the product can be obtained.

The most common catalyst compositions used for the Fischer-Tropsch process consist of iron or cobalt, supported or unsupported, containing optional promoters or additives. If, however, the process is being used to convert a synthesis gas derived from natural gas, cobalt based catalyst formulations are preferred to iron based catalysts because of their greater carbon efficiency.

The "classic" cobalt, thoria, magnesia on kieselguhr catalyst is useful for distillate production producing considerable amounts of hydrocarbons boiling in both distillate and wax fractions. The wax can then be hydrocracked to increase the amount of distillate produced. The hydrocarbons are also essentially linear paraffins which give a high quality, high cetane rated distillate. Similar products result from silica, alumina and silica-alumina supported cobalt catalysts.

In order to produce hydrocarbons suitable for use as gasoline, bifunctional catalyst systems have been introduced, in which the Fischer-Tropsch active metal is supported on a zeolite, so as to utilise the shape selective and acidic properties of the zeolite to limit the chain length of the product and produce a gasoline fraction of enhanced octane number by increasing the levels of branching and/or aromatics in the product. Zeolites such as Zeolite Y and ZSM-5 have been used as such supports.

US Patent 4 086 262 (Mobil Oil Corporation) describes the use of zeolites such as ZSM-5 as supports for Fischer-Tropsch metals including iron, cobalt, nickel, ruthenium, thorium and osmium, to produce an aromatic rich product from synthesis gas.

Australian Patent Application AU 34883/84 (Union Carbide Corporation) describes the use of catalyst compositions consisting of steam-stabilised Zeolite Y as a support for conventional Fischer-Tropsch metals such as iron or cobalt. These compositions enhanced the amount of product boiling in the liquid fuel range as well as branching and aromatisation in the products.

However, these processes based on bifunctional catalysts still produce an aromatic rich product, which would be undesirable for use in a reformulated gasoline. But by regulating the operating conditions used in conjunction with certain zeolite supported catalyst systems products with no or only very low levels of aromatics can be made.

Australian Patent Application AU 88929/82 (U.S. Department of Energy) describes a catalyst composition of cobalt, promoted with thoria, on a ZSM-5 type zeolite support which is used to produce high octane liquid hydrocarbon products containing branched aliphatic hydrocarbons rather then aromatics to impart high octane numbers. This catalyst when operated at approximately 280°C produced a liquid hydrocarbon product which contained only approximately 3% aromatics.

By operating zeolite supported cobalt catalysts at slightly lower temperatures (220-270°C) we have found that the liquid hydrocarbon product is limited to essentially gasoline and distillate fractions, is highly branched, and that the gasoline fraction is more highly branched than the corresponding distillate fraction. This is described in our Australian Patent Application AU 26671/88. Subsequent NMR studies of the product have shown that at these lower reaction temperatures no detectable quantities of aromatics are formed.

As these Fischer-Tropsch naphthas are already of relatively high octane rating, contain little or no detectable quantities of aromatics, and are limited to essentially the liquid fuel range, treatment of these naphthas to form a reformulated gasoline blendstock is relatively simple and cost effective.

The use of these naphthas as reformulated gasoline blendstocks is even more attractive as they can be produced from such an abundant and relatively inexpensive source as natural gas.

It is thus an object of the invention to produce from synthesis gas a non-aromatic, highly branched Fischer-Tropsch naphtha, and to further upgrade this naphtha to an improved high octane blendstock for reformulated gasoline.

BRIEF SUMMARY OF THE INVENTION

Accordingly the present invention provides a process for producing gasoline blendstock which process comprises contacting synthesis gas comprising carbon monoxide and hydrogen with a catalyst comprising cobalt supported on a ZSM-5 type zeolite at a temperature in the range from 220°C to 280°C to produce a naphtha, fractionating the naphtha to remove butanes and hydrocarbons boiling at a temperature in excess of 174°C and isomerising normal paraffins contained in the fractionated naphtha to produce a gasoline blendstock.

DETAILED DESCRIPTION OF THE INVENTION

The Fischer-Tropsch naphthas for use in this invention consist predominantly of hydrocarbons in the gasoline range have high levels of branching and contain little or no detectable quantities of aromatics.

These naphthas are obtained from synthesis gas via a variant of the Fischer-Tropsch process. The synthesis gas comprises substantial proportions of carbon monoxide and hydrogen, but may also contain carbon dioxide, water, methane and nitrogen. The synthesis gas may be obtained from carbonaceous sources such as natural gas, coal, oil shale and petroleum hydrocarbons by known processes such as partial oxidation, gasification and steam reforming. The relative concentrations of the gaseous components depend on the source of the synthesis gas and the process by which it is obtained. Hydrogen to carbon monoxide molar ratios of synthesis gases for use in the present invention may lie in the range from 0.2 to 6.

We are particularly interested in using natural gas derived synthesis gas as a means of utilising Australia's abundant natural gas reserves, and thus preferred synthesis gases have hydrogen to carbon monoxide molar ratios in the range from 1 to 3.

When the synthesis gas is natural gas-derived, cobalt is the Fischer-Tropsch active metal used in the Fischer-Tropsch catalyst formulations to produce these naphthas, and is preferably present in an amount of 1 to 50 weight percent based on the total weight of the catalyst composition.

As a high octane gasoline is being targeted, a shape selective, acidic zeolite is required as the catalyst support. Zeolites of reasonably high silica to alumina ratios, i.e. 10 or higher, fulfil this requirement. These zeolites are exemplified by the ZSM-5 type zeolites which include ZSM-5, ZSM-11, ZSM-12, ZSM-35, ZSM-38 and other similar materials. Particularly favoured are the small crystal variations of these ZSM-5 type zeolites, as described in our Australian Patent 613 813, in which ZSM-5 type zeolites of 5μm or less, or more preferably 1μm or less, are used as supports to produce a highly branched, and hence high octane, liquid hydrocarbon product. The ZSM-5 type zeolite is preferably present in the formulation in an amount of from 10 to 98 weight percent.

It is known to those skilled in the art that thoria and/or other materials such as magnesia, beryllium oxide, alumina, uranium oxides and manganese can be used as promoters for cobalt Fisher-Tropsch catalysts in order to improve catalyst activity and selectivity. Other additives or promoters such as chromium, scandium and praseodymium have also been shown to be beneficial in these compositions in Australian Patent Application Serial No. 638741 and our co-pending International patent applications PCT/AU92/00457 and PCT/AU93/00067, Australian patent applications AU 62238/90, PK7995 and PL0941. Presence of these promoter materials is optional, but preferred. Thoria and/or other promoters/additives can be present in an amount of from 0.01 to 25 weight percent, more preferably from 0.05 to 5 weight percent.

The cobalt, promoter and other additives may be loaded onto the support by any of the methods known to those skilled in the art. These methods include:

(i) mixing the appropriate oxides and support,

(ii) precipitating the metals from solution as carbonates, followed by drying, calcining and mixing the resulting oxides with the support.

(iii) precipitating the metals as carbonates on the support, followed by drying and calcination,

(iv) impregnating the support with appropriate metal carbonyl solutions and/or appropriate soluble metal salt solutions, followed by drying and calcination. Aqueous or organic solutions may be used as appropriate,

(v) combinations of the above methods.

As also described in our co-pending International Patent Application PCT/AU93/00067, improved results are obtained by preparing the catalysts by method (iv) above, and thus this method is particularly preferred.

Before use in synthesis gas conversion, the catalyst is reduced or activated. As is known by those skilled in the art, hydrogen, synthesis gas or another reductant may be used for this reduction step under conditions of elevated temperature and pressures of from atmospheric to the pressures used in the synthesis. Typical reduction temperatures are of the order of 250-350°C, with typical pressures of from atmospheric to 3.5 MPa.

The Fischer-Tropsch process can be performed over a wide range of temperatures, pressures and space velocities. However, there are some limitations on the temperature range used if the required product is to be obtained. In order for the zeolite to be effective in producing branched hydrocarbons the system must be at a temperature at which isomerisation reactions can occur on the zeolite. This places a lower limit of 200°C on the reaction. As the temperature is increased to 280°C aromatics formation begins. As the temperature is further increased other undesirable side reactions begin to occur, including cracking, methanation, carbon deposition and the water gas shift. Preferably the reaction temperature is maintained in the range from 220 to 280°C, and most preferably in the range from 220 to 270°C.

Typical pressures used in the synthesis are of the order of from 0 to 5 MPa, usually from 1 to 3.5 MPa, whilst typical space velocities are at GHSV's (Gas Hourly Space Velocities) of the order of from 10 to 10000 hr^{-1}, usually from 50 to 5000 hr^{-1}.

The first step in the treatment of the Fischer-Tropsch naphtha is fractionation.

Controls on the volatility of the product will require the removal of C_4 hydrocarbons. The Fischer-Tropsch naphthas used in the invention generally contain of the order of 1-2% C_4 hydrocarbons. However, any C_4's removed can be converted to isobutylenes for MTBE production.

The endpoint of the gasoline will also have to be controlled to avoid emissions of volatile organic compounds. In most refineries the endpoint is usually 216°C (412°F) or higher. This corresponds to a C_{12} cut-off. The endpoints of the Fischer-Tropsch naphthas used in this invention vary with the catalyst and process conditions used, but generally 60-99% of the liquid hydrocarbon product boils under 216°C. In fact, generally

50-98% of the product boils under 174°C (345°F), or the C_{10} cut-off. Due to emission reductions which can be achieved by dropping the endpoint to C_{10}, the product boiling above 174°C is separated. This separated fraction can be used as a distillate blendstock or be selectively cracked for inclusion into the gasoline pool.

The fractionated Fischer-Tropsch naphtha now consists of iso-paraffins, normal paraffins, iso-olefins and normal olefins boiling between C_5 and C_{10}. This naphtha may contain of the order of 10-60% normal paraffins, 1-30% normal olefins and 50-80% iso-paraffins and iso-olefins, with preferred naphthas typically containing 15-25% normal paraffins, 1-10% normal olefins and 65-75% iso-paraffins and iso-olefins.

At this point, because high olefin contents are undesirable in reformulated gasolines, naphthas with high olefin contents may have to be hydrotreated to reduce these levels. This would give a product containing predominantly iso-paraffins (65-75%) and normal paraffins (25-30%).

Finally, because of the low octane value of the remaining n-paraffins isomerisation to higher octane iso-paraffins is desirable to further boost the octane rating of the product. Although a once through, or single-pass isomerisation process can be used, it is preferable to use a process which utilises recycle to further convert any unconverted normal paraffins. This can be done by adding a molecular sieve adsorption step to the isomerisation process so that normal paraffins can be separated from the iso-paraffins. The normal paraffins can then be recycled through the isomerisation and separation steps to extinction. This process can be reactor-lead, where the fresh feed and any recycle are fed to the isomerisation reactor before separation of non-normals, or adsorber-lead, where the fresh feed is fed to the adsorber before isomerisation. However, in the process of our invention, as the feed to be isomerised is normally of low normal paraffin content, it is preferable to first extract these by adsorption, thus requiring a smaller isomerisation unit.

An example of such a process is the Total Isomerisation Process (TIP) licensed by UOP (formerly Union Carbide Corporation) which is further described in "Handbook of Petroleum Refining Processes" edited by R.A. Meyers (McGraw-Hill, New York, 1986). This process combines UOP's separation technology known as IsoSiv, with Shell's Hysomer isomerisation process. In IsoSiv normal paraffins are separated from a hydrocarbon mixture by selective adsorption on a zeolite molecular sieve. This material has uniform pores of such a size as to allow the normal paraffins to pass through the pore openings into the zeolite cavities where they are adsorbed. Larger hydrocarbons such as iso-paraffins cannot enter the zeolite pore structure for adsorption and are removed. In TIP desorption of the normal paraffins is effected by stripping with recycle hydrogen, and then passing the stripped normal paraffins in the hydrogen stream directly to the isomerisation reactor. In this reactor isomerisation of normal paraffins to iso-paraffins in a hydrogen stream occurs over an acidic metal loaded molecular sieve. As the degree of isomerisation is thermodynamically controlled, only partial isomerisation of normal paraffins is obtained and the stream is recycled to separate the iso-paraffins formed and to further isomerise the normal paraffins. This process operates in the vapour phase at temperatures of 200 to 370°C, and pressures of 1.4 to 3.4 MPa.

The product from this isomerisation process is a high octane, highly isomerised naphtha, excellent as a reformulated gasoline blendstock. Its other properties include low volatility, very little or no detectable aromaticity, and because of its low endpoint and low aromaticity it causes minimum emissions of organic compounds.

In order to produce a reformulated gasoline meeting the requirements of the Clean Air Act, oxygen containing compounds such as MTBE or other ethers or alcohols will have to be added to this blendstock so as to bring the oxygen content up to a minimum of 2%. This would have the effect of further increasing the octane rating of the product. The butanes removed in the fractionation step could be used in MTBE production.

The attached FIGURE further illustrates an embodiment of the invention. A synthesis gas stream 1 comprising substantially hydrogen and carbon monoxide with a preferred H_2 to CO molar ratio in the range from 1 - 3 is passed to a Fischer-Tropsch reactor 2 containing an activated cobalt on ZSM-5 type zeolite catalyst, preferably a promoted, activated cobalt on small crystal ZSM-5 type zeolite catalyst at 220-280°C, 0-5MPa with a GHSV of 10 - 10,000 hr^{-1}, preferably at 220-270°C, 1-3.5MPa with a GHSV of 50 - 5,000hr^{-1}.

The Fischer-Tropsch naphtha 3 exiting from this reactor, typically with a RON (Research Octane Number) of the order of 65, is then passed to a fractionator 4 for removal of C_4 hydrocarbons 5 and all hydrocarbons with a boiling point above 174°C 6. The C_4 hydrocarbons removed can be used to produce MTBE for incorporation into reformulated gasoline, while the higher hydrocarbons can be used as a distillate blendstock or be selectively cracked for inclusion into the gasoline pool.

The fractionated Fischer-Tropsch naphtha 7 may then be passed to a hydrotreating unit 8 along with additional hydrogen 9 in order to reduce its olefin content.

This optionally hydrotreated feed 10 is then isomerised, most preferably in an adsorber-lead isomerisation process with recycle, whereby the feed 10 is passed to an adsorption bed 11 where the normal paraffins are adsorbed, whilst the iso-paraffins 12 pass through for collection. Desorption of the normal paraffins is effected by stripping with hydrogen (make up hydrogen 13 and recycle hydrogen 16).

The normal paraffins in the hydrogen stream 14 are then passed to the isomerisation reactor 15 where the normal paraffins are partially isomerised to iso-paraffins and the effluent stream 16 containing iso-paraffins, normal paraffins and recycle hydrogen is recycled to the adsorption bed 11 to separate the iso-paraffins formed and to further isomerise the normal paraffins in the isomerisation reactor 15. The isomerisation and adsorption steps are operated at 200 to 370°C and 1.4 to 3.4 MPa.

The product obtained is a highly isomerised, non-aromatic naphtha, with a low endpoint and volatility. It's RON is of the order of 90.

Although the invention has been described with preferred embodiments it will be clearly understood that the invention in its general aspects is not limited to the specific details described hereinabove.

CLAIMS:

1. A process for producing gasoline blendstock which process comprises contacting synthesis gas comprising carbon monoxide and hydrogen with a catalyst comprising cobalt supported on a ZSM-5 type zeolite at a temperature in a range from 220°C to 280°C to produce a naphtha, fractionating the naphtha to remove butane and hydrocarbons boiling at a temperature in excess of 174°C thereby producing a fractionated naphtha and isomerising normal paraffins contained in the fractionated naphtha to produce a gasolene blendstock.

2. A process according to Claim 1, wherein the catalyst contains from 1 to 50 weight per cent of cobalt based on the total weight of catalyst.

3. A process according to Claim 1, wherein the catalyst contains from 10 to 98 percent by weight of the ZSM-5 type zeolite based on the total weight of catalyst.

4. A process according to Claim 2, wherein the catalyst contains from 0.01 to 25 weight per cent of a promoter based on the total weight of catalyst.

5. A process according to Claim 1, wherein the catalyst is prepared by impregnating the ZSM-5 type zeolite with a solution of cobalt carbonyl.

6. A process according to Claim 1, wherein the synthesis gas is contacted with the catalyst at a temperature in a range from 220°C to 270°C.

7. A process according to Claim 1, including passing the fractionated naphtha to a separation unit for separating iso-paraffins from normal paraffins to obtain a

stream of normal paraffins and a stream of iso-paraffins, passing the stream of normal paraffins through an isomerization unit for isomerising normal paraffins to iso-paraffins to form an isomerised stream of paraffins and passing the isomerised stream of paraffins through the separation unit.

8. A process according to Claim 1, wherein the normal paraffins contained in the fractionated naphtha are isomerised by selectively absorbing the normal paraffins on a zeolite molecular sieve, desorbing the normal paraffins from the zeolite molecular sieve with hydrogen thereby obtaining a stream of normal paraffins and hydrogen, passing the stream of normal paraffins and hydrogen to an isomerisation reactor, passing the stream of normal parraffins and hydrogen over an acidic, metal-loaded molecular sieve at a temperature in a range from 200°C to 370°C and a pressure in a range from 1.4 to 3.4 MPa to produce a product stream and passing the product stream to the zeolite molecular sieve.

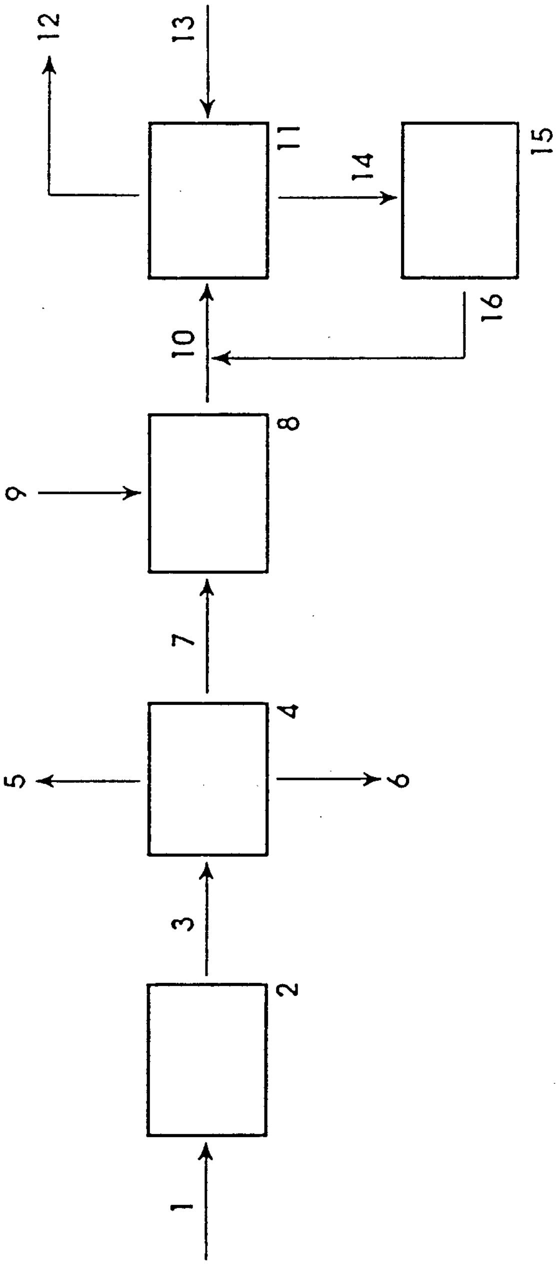

FIGURE 1

SUBSTITUTE SHEET

INTERNATIONAL SEARCH REPORT

International application No.
PCT/AU 93/00433

A. CLASSIFICATION OF SUBJECT MATTER

Int. Cl.^{5} C07C 1/04 // C10G 2/00

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 C07C 1/04

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched
AU: IPC as above

Electronic data base consulted during the international search (name of data base, and where practicable, search terms used)
FILE WPAT (DERWENT DATABASE) Keywords: Synthesis gas; cobalt; zeolite
FILE CASM (CHEMICAL ABSTRACTS) Keywords: Synthesis gas; cobalt; zeolite

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to Claim No.
A,P	AU,A, 16040/92 (SHELL INTERNATIONAL RESEARCH MAATSCHAPPIJ B V) 12 November 1992 (12.11.92)	1-8
A	AU,B, 62238/90 (638741) (THE BROKEN HILL PROPRIETARY COMPANY LIMITED) 14 March 1991 (14.03.91)	1-8
A	US,A, 4659743 (RAO et al.) 21 April 1987 (21.04.87)	1-8

☒ Further documents are listed in the continuation of Box C.

☒ See patent family annex.

*	Special categories of cited documents :
"A"	document defining the general state of the art which is not considered to be of particular relevance
"E"	earlier document but published on or after the international filing date
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"&"	document member of the same patent family

Date of the actual completion of the international search 9 November 1993 (09.11.93)	Date of mailing of the international search report 15 NOV 1993 (15. 11. 93)
Name and mailing address of the ISA/AU AUSTRALIAN INDUSTRIAL PROPERTY ORGANISATION PO BOX 200 WODEN ACT 2606 AUSTRALIA Facsimile No. 06 2853929	Authorized officer G R Peters G R PETERS Telephone No. (06) 2832244

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	**Citation of document, with indication, where appropriate of the relevant passages**	**Relevant to Claim No.**
A	INDUSTRIAL & ENGINEERING CHEMISTRY PRODUCT RESEARCH AND DEVELOPMENT VOLUME 23, No. 4, pages 513-514 (1984) Shamsl, A, et al "Zeolite-Supported Cobalt Catalysts for the Conversion of Synthesis Gas to Hydrocarbon Products"	1-8

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.

Patent Document Cited in Search Report	Patent Family Member		
AU,A, 16040/92	CA,A, 2068026 NO,A, 921777	EP,A, 512635 ZA,A, 9203236	GB,A, 9109747
AU,B, 62238/90	CA,A, 2025101 US,A, 5126377	GB,A, 2236262	NZ,A, 235247
US,A, 4659743	AU,B, 575016	CA,A, 1177464	JP,A, 58071987

END OF ANNEX