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(54) Title: PROCESS

(57) Abstract: The present invention relates to a process for the production of branched chain hydrocarbons from methanol and/or dimethyl ether, which process comprises contacting, in a reactor, methanol and/or dimethyl ether with a catalyst comprising metal halide selected from rhodium halide, iridium halide and combinations thereof.



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PROCESS

This invention relates to a process for preparing branched chain hydrocarbons, in particular to a process for preparing a branched chain hydrocarbon product comprising
5 triptane.

Branched chain hydrocarbons may be synthesised by a number of routes. In particular, mixtures of branched chain hydrocarbons may be formed by homologation of methanol and/or dimethyl ether in the presence of a zinc halide catalyst, as described, for example in GB 1,547,955, US 2,492,984, US 3,969,427, US 4,059,646, US 4,059,647, US
10 4,249,031 and WO02/70440.

US 4,249,031, for example, describes a process for the preparation of a hydrocarbon mixture by contacting one or more oxygen-containing organic compounds, such as methanol, with one or more zinc halides.

US 4,059,647, for example, describes a process for the production of triptane (2,2,3-trimethylbutane) comprising contacting methanol, dimethyl ether or mixtures thereof with
15 zinc iodide.

Triptane is a branched chain hydrocarbon of high octane number, which can be used in unleaded aviation gasoline and unleaded motor gasoline (see, for example, WO 98/22556 and WO 99/49003).

20 We have now found an alternative and/or improved process to produce branched chain hydrocarbons from methanol and/or dimethyl ether.

According to a first aspect, the present invention provides a process for the production of branched chain hydrocarbons from methanol and/or dimethyl ether, which process comprises contacting, in a reactor, methanol and/or dimethyl ether with a catalyst
25 comprising a metal halide selected from rhodium halide, iridium halide and combinations thereof.

In the present invention the reaction of methanol and/or dimethyl ether produces reaction products comprising branched chain hydrocarbons

Where the metal halide comprises rhodium halide, the rhodium halide is preferably
30 RhX_3 , wherein X is a halide selected from Cl, Br and I, and combinations thereof. More preferably the rhodium halide is RhI_3 , although other rhodium compounds may be present

in the reactor. Where the metal halide comprises iridium halide, the iridium halide is preferably IrX_3 , wherein X is a halide selected from Cl, Br and I, and combinations thereof. More preferably the iridium halide is IrI_3 , although other iridium compounds may be present in the reactor.

5 The metal halide may be introduced to reactor in the form of a compound comprising both the metal, M, and at least one halogen atom, X. Preferably, the metal halide is introduced to the reactor as MX_3 , wherein X is a halide selected from Cl, Br and I, and combinations thereof. Most preferably the metal halide is introduced to the reactor as MI_3 . The metal halide may be introduced to the reactor the form of an anhydrous salt or may be
10 added in the form of a solid hydrate.

 Alternatively, or additionally, the metal halide may be formed in-situ in the reactor, for example, by reaction of a suitable metal source with a halide source in the reactor. Suitable metal sources include, for example, metal compounds such as oxides, hydroxides, acetates, alkoxides, nitrates and sulphates. Suitable halide sources include hydrogen halides
15 and alkyl halides, for example, methyl halides.

 The process of the present invention may be performed in the presence of metal halides other than rhodium and/or iridium, or may be performed in the substantial absence of metal halides other than rhodium and/or iridium.

 For example, as well as the metal halide selected from rhodium halide, iridium halide
20 and combinations thereof, the reactor may also contain zinc halide, such as zinc iodide. Alternatively, the process of the present invention may be performed in the substantial absence of zinc halide.

 Similarly, as well as the metal halide selected from rhodium halide, iridium halide and combinations thereof, the reactor may also contain indium halide, such as indium
25 iodide.

 In addition to methanol and/or dimethyl ether reactants, there may also be introduced to the reactor additional feedstock components. Suitable additional feedstock components include hydrocarbons, halogenated hydrocarbons and oxygenated hydrocarbons, especially olefins, dienes, alcohols and ethers. The additional feedstock components may be straight
30 chain, branched chain or cyclic compounds (including heterocyclic compounds and

aromatic compounds). In general, any additional feedstock component in the reactor may be incorporated in the products of the reaction.

Certain additional feedstock components may advantageously act as initiators and/or promoters for the reaction to produce branched chain hydrocarbons.

5 Thus, in one preferred embodiment, the reactor also contains one or more compounds that can act as initiators for the reaction to produce branched chain hydrocarbons. Suitable initiators are preferably one or more compounds having at least 2 carbon atoms selected from alcohols, ethers, olefins and dienes.

10 Preferred initiator compounds are olefins, alcohols and ethers, preferably having 2 to 8 carbon atoms. Especially preferred initiator compounds are 2-methyl-2-butene, 2,4,4-trimethylpent-2-ene, ethanol and MTBE.

15 In a further preferred embodiment, there is also present in the reactor one or more promoters selected from one or more of hydrogen halides and alkyl halides of 1 to 8 carbon atoms. Methyl halides and/or hydrogen halides are generally preferred. For the production of branched chain hydrocarbons from dimethyl ether (DME), methyl halides are especially preferred promoters. Preferably the halide of the promoter is the same element as the halide of the metal halide catalyst.

20 Additional feedstock components, including compounds that may act as initiators and/or promoters, may be introduced as "fresh" compounds or mixtures of compounds to the reactor, but may also be formed in-situ in the reactor during the reaction to produce branched chain hydrocarbons. For example, olefins and dienes that may be formed in the reaction may act as initiators. As a further example, alkyl halides, such as methyl iodide, that may be formed may act as promoters. Thus, in one preferred embodiment, either alternatively to or in addition to any "fresh" additional feedstock components introduced to
25 the reactor, additional feedstock components, and especially initiators and/or promoters, may be introduced in to the reactor as components of a suitable recycle stream. Suitable recycle streams may be obtained, for example, by recycle of a portion of a product stream from the reactor, preferably by recycle of at least a portion of a by-product stream formed after separation of desired branched chain hydrocarbons, such as triptane, and any other
30 useful products from said reactor product stream.

As with additional feedstock components in general, any initiators and/or promoters introduced to the reactor may be incorporated in the reaction products.

Water is formed during the reaction of methanol and/or dimethyl ether to produce branched chain hydrocarbons. Optionally, additional water may also be introduced to the
5 reactor.

The process of the present invention may be either a gas or liquid phase process. However, advantageously, the process is operated substantially in the liquid phase.

Accordingly, in a second aspect, the present invention provides a process for the production of branched chain hydrocarbons from methanol and/or dimethyl ether, which
10 process comprises contacting, in a liquid phase reaction composition in a reactor, methanol and/or dimethyl ether with a catalyst comprising a metal halide selected from rhodium halide, iridium halide and combinations thereof.

In a preferred embodiment of the second aspect of the present invention the liquid reaction composition also comprises at least one additional feedstock component, and most
15 preferably comprises at least one initiator and/or at least one promoter, wherein said additional feedstock components, initiators and promoters are as defined herein.

The process of the second aspect of the present invention allows branched chain hydrocarbons to be formed in a liquid phase reaction at relatively low temperatures, such as 100°C to 300°C.

20 In a third aspect, the present invention also provides a continuous or semi-continuous process for the production of branched chain hydrocarbons from methanol and/or dimethyl ether, which process comprises contacting, in a liquid phase reaction composition in a reactor, methanol and/or dimethyl ether with a catalyst comprising a metal halide selected from rhodium halide, iridium halide and combinations thereof, and at a temperature of at
25 least 100°C, to produce a product mixture comprising (i) methanol and/or dimethyl ether and (ii) a hydrocarbon reaction product comprising branched chain hydrocarbons, and in which process the catalyst is maintained in the reactor in an active form and in an effective concentration.

The catalyst comprising a metal halide may be maintained in an active form and in an
30 effective concentration in the reactor by recycling to the reactor, one or more promoter

compounds as defined previously, such as, for example, hydrogen iodide and/or methyl iodide from downstream product recovery stage(s).

In a preferred embodiment of the third aspect of the present invention the liquid reaction composition also comprises at least one further additional feedstock component, and more preferably comprises at least one initiator, which has been recycled from downstream product recovery stage(s), wherein said additional feedstock components and initiators are as defined herein.

Preferably, the processes of the present invention are performed substantially in the liquid phase to produce a product mixture comprising methanol and/or dimethyl ether in a first liquid phase and the hydrocarbon reaction product comprising branched chain hydrocarbons in a second liquid phase. However, it may be necessary to cool the product mixture to form the first and second liquid phases. The hydrocarbon reaction product is then usually separated from the mixture.

The first liquid phase is typically a hydrophilic phase comprising at least one of water, methanol and dimethyl ether. The first liquid phase may also comprise the catalyst comprising metal halide. The catalyst may be completely dissolved or there may also be a solid phase present and the catalyst may be partially dissolved in the first liquid phase. The first liquid phase and any solid phase may be retained in the reactor. Alternatively, it may be removed and processed to recover water prior to recycle. Alternatively or additionally, the catalyst may be recovered from the first phase, and optionally, regenerated for re-use.

The second liquid phase, if present, is typically a hydrophobic phase comprising the branched chain hydrocarbon product. Other, by-product, hydrocarbon compounds may also be present in the second phase. Examples of possible by-product hydrocarbon compounds include non-branched paraffinic and olefinic hydrocarbons, and aromatic hydrocarbons. The hydrophobic phase is generally less dense than the hydrophilic phase. The hydrophobic phase may also comprise, dissolved therein, one or more of methanol, dimethyl ether, methyl halide (e.g. iodide) and water.

Preferably, a mixture of methanol and dimethyl ether is used in the present invention. This has an advantage that the reaction of dimethyl ether and methanol produces less water than is produced from reaction of methanol alone. If methanol is used in downstream stages of the overall process for the production of branched chain hydrocarbons, for

example in scrubbing gaseous effluent or aiding separations, then there may be a limit to the amount of methanol which can be substituted by dimethyl ether in the process if methanol and/or dimethyl ether are recycled from the downstream processes to the reactor.

5 In the processes of the present invention the methanol and/or dimethyl ether is usually contacted with the metal halide catalyst at a temperature of at least 100°C. Preferably, the methanol and/or dimethyl ether is contacted with the metal halide at a temperature of 100 to 300 °C, preferably 100-250°C, more preferably 120 to 250 °C.

10 The reaction time of the processes of the present invention is usually 0.1-9 hrs, for example, 0.3-3hrs. Lower temperatures tend to require longer reaction times. Reaction temperatures are usually lower for dimethyl ether than methanol. The times may be the reaction times in a semi-continuous reaction, or residence time (including average residence time) for continuous processes. The reaction of the processes of the present invention may be monitored for conversion of the methanol or dimethyl ether by periodic sampling in the reaction (for a semi-continuous or continuous process) or in reaction
15 effluent for a continuous process, and then analysis by an appropriate technique e.g. gas liquid chromatography or mass-spectroscopy.

The reaction of the processes of the present invention is usually performed at elevated pressure such as 1 – 100 barg, preferably 5-100 barg, such as 50-100 barg. The pressure may be autogenous, or may be provided also by the presence of an added inert gas,
20 such as nitrogen or argon, and/or preferably by the presence of added hydrogen, as further described below.

The ratio of methanol and/or dimethyl ether and water to each other and to the metal halide catalyst employed in the reaction may vary widely. Since methanol, dimethyl ether and water may be present in one or more liquid phases in the reactor and the vapour phase,
25 and the metal halide may be present in liquid or solid phase it is convenient to express the concentrations of methanol, dimethyl ether, water and catalyst components as relative weight parts in the reactor excluding any hydrocarbon components or phase. For example, for a total (excluding hydrocarbon components or phase) of 100 weight parts of methanol, dimethyl ether, water and catalyst, the catalyst is preferably greater than 50 parts and less
30 than 99 parts, more preferably greater than 70 parts and less than 95 parts and most preferably greater than 80 parts and less than 90 parts. The water is preferably less than 50

parts and greater than 0, more preferably less than 25 parts and most preferably less than 10 parts. The balance of methanol and dimethyl ether will be to make 100 weight parts. The hydrocarbon components/phase will be additional to this. The ratio of methanol to dimethyl ether may vary from being all dimethyl ether through to all methanol. If
5 preferred, the composition may be chosen to maximise the solubility of the catalyst in the liquid phase or phases at the reaction temperature but operation of the invention is not limited to reactor compositions where no solid phase is present.

Preferably, the process is performed in the substantial absence of added water, especially with methanol as reactant. As water is a co-product of the process, it may be
10 removed from the reactor as the reaction proceeds suitably to maintain a steady state concentration in the process.

It may also be possible to remove water from the reactor using techniques such as for example, with desiccants, such as magnesium silicate or molecular sieves e.g. zeolites such as 3A or 13X usually in a non acidic form, e.g. in a metal form when the metal may be an
15 alkali metal, for example, Na or K.

It may be useful to recycle some of the separated water product as a wash stream to wash out any catalyst dissolved in the second liquid phase.

The reaction of the present invention may be performed in the presence of hydrogen. Hydrogen may be introduced into the reactor as fresh feed and/or as a component in a
20 recycle stream. Thus, hydrogen may be introduced to the reactor as a separate feed stream, or together with the catalyst and/or one of the other reactants.

It is known to perform reactions in the presence of zinc halide as a homologation catalyst and a separate hydrogenation catalyst, such as catalyst comprising a Group VIII metal, as described in WO 02/70440. The use of a catalyst comprising metal halide
25 selected from rhodium halide, iridium halide and combinations thereof has the advantage that said metal may also have hydrogenation activity.

The reaction of the present invention may also be performed in the presence of a separate hydrogenation catalyst, which may be soluble or insoluble. The separate hydrogenation catalyst preferably comprises a supported Group VIII metal (CAS notation,
30 as defined in the Periodic Table of the Elements in Advanced Inorganic Chemistry, 5th Edition, by Cotton and Wilkinson), for example, Ni, Rh, Pd, Os, Ir, Pt, and Ru on an inert

support, such as active carbon, for example, charcoal, or alumina, silica or silica/alumina. Preferred examples include catalysts consisting essentially of, or comprising ruthenium, nickel and/or palladium. Preferably, a Ru catalyst is employed, optionally, in the presence of Re. Amounts of the Group VIII metal in the supported catalyst may be 0.01-30% by weight (expressed as metal): for example, a supported Ni catalyst may comprise 0.01-10% or 10-30% wt Ni.

Preferred catalysts include Ru, Ni or Pd on carbon, Ru on alumina and Ru and Re (in relative wt amounts of 2-6:1) on C. A most preferred catalyst is Ru/C, for example, where the amount of Ru in the catalyst is 0.01-10 wt%.

The reaction of the present invention may be performed in the presence of carbon monoxide. Carbon monoxide may be introduced into the reactor as fresh feed and/or as a component in a recycle stream. Thus, carbon monoxide may be introduced to the reactor as a separate feed stream, or together with the catalyst and/or one of the other reactants. Where both hydrogen and carbon monoxide are introduced to the reactor it is especially desirable to use synthesis gas as a source of both. The presence of carbon monoxide in the reactor may lead to production of branched chain esters, as described, for example, in US 4,166,189. For the production of branched chain esters, the carbon monoxide, is preferably present in the reactor at a molar ratio of carbon monoxide to methanol of at least 0.25:1, more preferably at least 10:1.

The production of branched chain esters by inclusion of carbon monoxide in the reactor may be further enhanced by inclusion of one or more initiators and/or one or more promoters, as described above, especially by introduction to the reactor of one or more olefins.

In contrast to the above, where it is desired to introduce hydrogen to the reactor but to avoid or reduce the production of branched chain esters it is desirable to use hydrogen containing feed streams with only low carbon monoxide content, such as streams with a molar ratio of hydrogen to any carbon monoxide present of at least 5:1, and preferably hydrogen in the substantial absence of carbon monoxide.

The invention will be further described with respect to a process for the production of triptane as a desired branched chain hydrocarbon reaction product, it being understood that other branched chain hydrocarbons may be produced by the present invention.

In a continuous or semi-continuous process for the production of triptane, the methanol and/or dimethyl ether fed to the reactor may be introduced continuously or semi-continuously, preferably continuously.

In one embodiment, the second liquid phase, if present, is separated from the first liquid phase, and recovered from the reactor. The second liquid phase, if present, generally comprises the desired triptane product. The second liquid phase may also comprise triptene, which may be converted to the desired triptane product. Triptane is useful in the production of motor and aviation gasoline, especially, unleaded motor and unleaded aviation gasoline.

The second phase will also comprises other hydrocarbon compounds, such as other branched chain hydrocarbons. Said other hydrocarbon compounds may be recycled to the reactor as additional feedstock components, and may be incorporated into further reaction products, as previously described.

Alternatively, some or all of these other hydrocarbon compounds may also be useful in the production of motor and aviation gasoline. In addition, some of the other hydrocarbon compounds, especially by-product compounds, may be useful other than in the production of motor and aviation gasoline. Thus, instead of recycling, these compounds may be separated where useful elsewhere.

Typical useful compounds may include, for example, C₄ to C₈ branched chain alkanes (other than triptane) and C₄ to C₈ branched chain alkenes, such as iso-butene, iso-pentene and 2,3-dimethylbutene. Further useful compounds may include, for example, aromatic compounds, such as methyl-substituted benzene compounds, particularly tetramethylbenzenes and pentamethylbenzenes, which could, for example, be separated and subsequently used to produce xylenes, particularly p-xylene, which is useful as a feedstock for the manufacture of PTA.

Thus, the processes of the present invention may further comprise the step of recovering a second liquid phase from the reactor and recovering therefrom a triptane-containing hydrocarbon product. The recovered triptane-containing product may be employed as, or as an additive for, a motor or aviation gasoline, preferably, an unleaded motor or aviation gasoline. Preferably the second liquid phase may be purified, for example by distillation, to enhance its concentration of triptane. Optionally, at least one

motor or aviation gasoline additive may be added to the hydrocarbons recovered from the recovered second liquid phase.

In the processes of the present invention, there will also be present in the reactor a vapour phase. The vapour phase may comprise at least one of hydrogen, water vapour, hydrocarbons (including triptane), alkyl halides, methanol and/or dimethyl ether. In one embodiment, water is separated from the process by withdrawing at least some of the vapour phase from the reactor. The vapour may be condensed and purified, for example, by distillation, to enhance its concentration of triptane. The vapour phase may be purified by condensation and distillation to provide a product water stream clean enough for disposal, a hydrocarbon product comprising triptane and a recycle stream containing unreacted feed components.

In a preferred embodiment the processes of the present invention may be performed in an adiabatic reactor or a reactor with heat-removal cooling coils, which may remove up to 20 % of the heat of reaction. In a preferred embodiment of a continuous process, the reactor is provided with a feed inlet through which in use passes co-joined recycle gases, fresh methanol and/or dimethyl ether and recycle methanol. In use, the methanol and/or dimethyl ether reacts, in the reactor, in the presence of a catalyst comprising metal halide to produce a mixture comprising water, hydrocarbons (including triptane) and unreacted methanol. Preferably, the reactor contains a hydrophilic liquid phase comprising the metal halide catalyst, a second, hydrophobic liquid phase comprising hydrocarbons, and a vapour phase comprising water and triptane. Water is removed from the reactor by removing vapour phase from the reactor. Triptane product may be recovered from the reactor from the vapour phase and/or from the liquid phase(s) removed from the reactor. Any catalyst components (halide and optionally metal) removed from the reactor in process streams removed for product recovery are recycled to the reactor to maintain in the reactor an effective concentration of catalyst comprising metal halide.

Methanol and or dimethyl ether present in the recovered vapour phase may be recycled to the reactor.

Suitable reactors and processes are further described, for example, in WO 02/070440.

Where the hydrocarbon reaction product comprising triptane is to be used as a blending component for a gasoline it is preferably distilled first to concentrate the triptane

fraction, and any triptene fraction. Preferably, prior to use as a blending component for a gasoline the hydrocarbon reaction product is hydrogenated to convert any triptene and/or other alkenes to triptane and/or other alkanes.

There are a number of preferred ways in which the processes of the present invention
5 may be used, some of which are described below.

(A) The process of the present invention may involve reacting methanol and/or dimethyl ether and the metal halide, to form a mixture of methanol and/or dimethyl ether and a hydrocarbon reaction product comprising triptane. The hydrocarbon reaction product may then be separated from the methanol and/or dimethyl ether, from the metal halide or
10 both, for example, by separation as a different liquid phase or by distillation. The hydrocarbon reaction product may then be separately hydrogenated with hydrogen over a hydrogenation catalyst, for example, at a pressure of 1-10 bar and a temperature of 10-100°C, preferably, 10-50°C. The hydrogenation converts any triptene (and other alkenes) to triptane (and other alkanes).

15 (B) Alternatively, instead of separating the hydrocarbon reaction product before hydrogenating the product, the hydrogenation can be performed prior to separation. After hydrogenation the triptane and other alkanes can be separated by distillation from the methanol or dimethyl ether, which can be recycled for reuse.

(C) In another alternative, the reaction of the methanol and/or dimethyl ether with the
20 metal halide may be performed at least in part in the presence of hydrogen, either in the presence or absence of a separate hydrogenation catalyst. At the desired conversion point, the hydrocarbon reaction product can be separated from the metal halide, and optionally from the methanol and/or dimethyl ether, preferably followed by hydrogenation over a suitable catalyst, especially if no separate hydrogenation catalyst were used in the metal
25 halide reaction step. If desired, a hydrogenation catalyst may be used in both steps. If the hydrocarbon reaction product contains no triptene, then the hydrocarbon reaction product is preferably separated from the metal halide, and optionally the methanol and/or dimethyl ether without any further hydrogenation.

In all these three alternatives (A) to (C), co-product water is separated in a vapour
30 phase from metal halide catalyst which is retained in a liquid or solid phase.

The invention will now be illustrated with respect to the following examples:

Example 1

RhI₃ experiment

In a dry box, 0.484 g of RhI₃ (1 mmol, purchased from Strem Chemicals), 0.12 ml
5 of MeOH (3 equiv), and 10 μ L of octane were loaded in a heavy-walled Schlenk tube.

The tube was taken out of the dry box and immersed in a heated oil bath at the temperature and for the reaction time indicated in Table 1.

After the reaction was completed, the tube was removed from the oil bath and allowed to cool down to room temperature. Dodecane (1 ml) was added to the solid
10 mixture and the suspension filtered through Celite.

An aliquot of the solution was diluted 5 times and the mixture was analysed by GC, using the octane as an internal standard to determine yields (calculated with respect to the amount of "CH₂" introduced in the reaction).

The yields of triptane and hexamethylbenzene (HMB) are given in Table 1.

15 Example 2

IrI₃ experiment

The experiment of Example 1 was repeated except that 0.573 g of IrI₃ (1 mmol, purchased from City Chemicals) was used in place of the rhodium iodide.

The reaction temperatures and times, along with the triptane and HMB yields are shown in
20 Table 1.

Example 3

IrBr₃ experiment

The experiment of Example 1 was repeated except using 1.296 g of IrBr₃·xH₂O (3 mmol based on IrBr₃, purchased from City Chemicals) in place of the rhodium iodide, 0.24
25 ml of MeOH (2 equivalents) and 0.38 ml of MeI (2 equivalent) and 10 μ L of octane.

After filtration, an aliquot of the solution was diluted 10 times and the mixture was analysed by GC.

The reaction temperatures and times, along with the triptane and HMB yields are shown in Table 1.

TABLE 1

Example	Metal halide	Reaction Temp. (°C)	Reaction Time (h)	Triptane yield (%)	HMB yield (%)
1	RhI ₃	120	9	9.0	0.9
1	RhI ₃	200	3	5.5	3.8
2	IrI ₃	160	6	6.9	1.7
2	IrI ₃	200	3	9.2	4.2
3	IrBr ₃	160	6	7.2	5.1
3	IrBr ₃	200	3	6.0	6.0

5 The above examples show that both rhodium and iridium halides can act as homologation catalysts for the production of branched chain hydrocarbons, such as triptane, from methanol and/or dimethyl ether.

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Claims

1. A process for the production of branched chain hydrocarbons from methanol and/or
5 dimethyl ether, which process comprises contacting, in a reactor, methanol and/or dimethyl
ether with a catalyst comprising a metal halide selected from rhodium halide, iridium
halide and combinations thereof.
2. A process according to claim 1, wherein the metal halide comprises RhX_3 , wherein X
10 is a halide selected from Cl, Br and I, and combinations thereof.
3. A process according to claim 2, wherein the rhodium halide is RhI_3 .
4. A process according to claim 1, wherein the metal halide comprises IrX_3 , wherein X
15 is a halide selected from Cl, Br and I, and combinations thereof.
5. A process according to claim 4, wherein the iridium halide is IrI_3 .
6. A process according to claim 1, wherein the reactor also contains zinc halide and/or
20 indium halide.
7. A process according to claim 1, wherein, in addition to methanol and/or dimethyl
ether reactants, there is also introduced to the reactor additional feedstock components
selected from hydrocarbons, halogenated hydrocarbons and oxygenated hydrocarbons,
25 especially olefins, dienes, alcohols and ethers.
8. A process according to claim 7, wherein the reactor contains one or more compounds
that can act as initiators for the reaction to produce branched chain hydrocarbons said
initiators being one or more compounds selected from alcohols, ethers, olefins and dienes
30 having at least 2 carbon atoms.

9. A process according to claim 8, wherein the initiator compounds are olefins, alcohols and ethers having 2 to 8 carbon atoms.

10. A process according to claim 7, wherein there is also present in the reactor one or
5 more promoters selected from one or more of hydrogen halides and alkyl halides of 1 to 8 carbon atoms.

11. A process according to claim 1, wherein the process is operated substantially in the liquid phase.

10

12. A process according to claim 11, wherein the process is operated at temperatures in the range 100°C to 300°C.

13. A process according to claim 1, wherein the process is performed at an elevated
15 pressure in the range 1 – 100 barg.

14. A process according to claim 1, wherein the reaction is performed in the presence of hydrogen.

20 15. A continuous or semi-continuous process for the production of branched chain hydrocarbons from methanol and/or dimethyl ether, which process comprises contacting, in a liquid phase reaction composition in a reactor, methanol and/or dimethyl ether with a catalyst comprising a metal halide selected from rhodium halide, iridium halide and combinations thereof, and at a temperature of at least 100°C, to produce a product mixture
25 comprising (i) methanol and/or dimethyl ether and (ii) a hydrocarbon reaction product comprising branched chain hydrocarbons, and in which process the catalyst is maintained in the reactor in an active form and in an effective concentration.

16. A process according to claim 15, wherein the catalyst comprising metal halide is be
30 maintained in an active form and in an effective concentration in the reactor by recycling to the reactor one or more promoter compounds, selected from one or more of hydrogen

halides and alkyl halides of 1 to 8 carbon atoms, from downstream product recovery stage(s).

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INTERNATIONAL SEARCH REPORT

International Application No

PCT/US2005/029180

A. CLASSIFICATION OF SUBJECT MATTER
C07C1/20

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)
C07C

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

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

EPO-Internal, WPI Data, PAJ, BEILSTEIN Data, CHEM ABS Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP 0 040 914 A (MOBIL OIL CORPORATION) 2 December 1981 (1981-12-02) page 7, line 18 -----	1-16
A	US 4 851 606 A (RAGONESE ET AL) 25 July 1989 (1989-07-25) the whole document -----	1-16
A	US 4 059 647 A (WALD ET AL) 22 November 1977 (1977-11-22) cited in the application the whole document -----	1-16

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

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Date of the actual completion of the international search

21 December 2005

Date of mailing of the international search report

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INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/US2005/029180

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US 4059647	A	22-11-1977	NONE	