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(54) Title: PROCESS FOR MANUFACTURE OF INTERNAL OLEFINS

(57) Abstract: The present invention provides a process for producing internal olefins which comprises activating a catalyst composition comprising potassium carbonate or potassium acetate supported on a porous refractory oxide material by heating it under flow of an oxygen-containing gas and an inert gas, and isomerizing an alpha olefin in the presence of the catalyst composition.

PROCESS FOR MANUFACTURE OF INTERNAL OLEFINS

Field of the Invention

This invention relates to a process for the manufacture of internal olefins by catalytic double bond isomerization of alpha olefins.

Background of the Invention

Isomerized alpha olefins (internal olefins) can be used in a variety of applications including drilling base fluids, feedstocks to manufacture alkyl succinic anhydride for paper sizing applications and feedstocks to manufacture lubricant additives. There are many catalytic processes that can be used to isomerize alpha olefins to internal olefins. Two general classes of catalysts for these systems are solid acid and solid base catalysts.

A solid acid catalyst such as described in U.S. Published Application No. 2005/0070747 will not only isomerize alpha olefins to internal olefins (double bond isomerization), but also generally will skeletally isomerize the alpha olefins, thereby forming branched olefins. These types of solid acid catalysts can also dimerize and trimerize the olefins to form high molecular weight materials. In some applications, the properties of skeletally branched olefins and/or dimerized and/or trimerized olefins can have negative effects on the final product. For example, for drilling fluid applications, the presence of skeletal branching will impact the environmental performance of these products. Higher levels of branching will make products less biodegradable and cause them to have more toxicity to sediment dwelling organisms in cases where these products are discharged to the environment via the offshore discharge of cuttings. In addition, higher levels of dimers and trimers may have negative impacts on the kinematic viscosity of the products. Kinematic viscosity is an important property for

drilling fluid applications and the higher viscosity caused by the presence of dimers and/or trimers makes these products less desirable for this use.

For alkyl succinic anhydride applications, the presence of dimers and trimers may result in some portion of the product behaving as an inert in the reactions. This results in a yield loss for the user. Having an internal olefin free of dimer and trimer olefin would result in higher reaction yields when producing alkyl succinic anhydride products. High dimer and trimer content in such products could also result in viscosity problems. For lubricant additive applications, the presence of dimerized and trimerized olefins may result in a yield loss as these dimerized and trimerized olefins are much less reactive in the processes used to make lubricant additives.

Summary of the Invention

The present invention provides a process for producing internal olefins which comprises:

(a) activating a catalyst composition comprising potassium carbonate or potassium acetate supported on a porous refractory oxide material, preferably amorphous gamma alumina, preferably for 2 to 24 hours, by heating it to a temperature of at least 350°C and causing an oxygen-containing gas, preferably air, to flow through the catalyst composition at a gas linear velocity of at least 250 centimeters per minute and then causing an inert gas, such as nitrogen, argon, or helium, to flow through the catalyst composition at a gas linear velocity of at least 250 centimeters per minute, and

(b) contacting at least one alpha olefin with the activated catalyst composition.

In a preferred embodiment, the catalyst composition is activated under activation conditions of heat and gas flow defined by the formula

$$k(isom) = a + bT + cF > 0$$

wherein k(isom) is the isomerization rate constant, which preferably is at least 0.05 and more preferably 0.1 or more (units – cubic centimeters of olefin/cubic centimeters of catalyst·minute), T is the temperature in °C, F is the gas linear velocity in centimeters per minute, a is a constant with units of k(isom) and equals -0.12 for the potassium acetate catalyst and -0.21 for the potassium carbonate catalyst, b is a coefficient with units k(isom)/°C and equals 0.0004 for the potassium acetate catalyst and 0.0007 for the potassium carbonate catalyst, and c is a coefficient with units of k(isom)/ centimeters per minute and equals 0.00003 for the potassium acetate catalyst and 0.00002 for the potassium carbonate catalyst.

In a preferred embodiment, the activation temperature may range from 350 to 600°C. In a preferred embodiment, the activation gas linear velocity may range from 300 to 2000 centimeters per minute. In a preferred embodiment, the temperature in step (b) may range from 50 to 200°C. In a preferred embodiment, the process in step (b) is continuous and the alpha olefin flow rate is a weight hourly space velocity of from 0.1 to 20.

Detailed Description of the Invention

The alpha olefin (1-alkene) to be isomerized by the process of the present invention may be linear or branched and may also contain a cycloaliphatic or aromatic ring structure. For many end uses, linear alpha olefins are preferred. Specific, but non-limiting, examples of suitable

1-alkenes for use in the present invention include at least one of 1-pentene, 3-methyl-1-butene, 2-methyl-1-pentene, 4-methyl-1-pentene, 1-hexene, 1-heptene, 1-octene, 2-methyl-1-octene, 2-ethyl-1-hexene, 5-methyl-1-heptene, 1-nonene, 1-decene, 1-undecene, 1-dodecene, 2-methyl-1-dodecene, 1-tetradecene, 2-methyl-1-tetradecene, 1-hexadecene, 2-methyl-1-hexadecene, 5-methyl-1-hexadecene, 1-octadecene, 2-methyl-1-octadecene, 1-eicosene, 2-methyl-1-eicosene, 1-docosene, 1-tetracosene, 1-hexacosene, vinylcyclohexane and 2-phenyl-1-butene, although the present invention is in no way limited to these examples. Examples of commercially available alpha olefins that may be utilized include, but are not limited to Neodene® 2024 (C_{20-24}), Neodene® 16 (C_{16}), Neodene® 18 (C_{18}), and Neodene® 1618 (C_{16-18}) olefins available from Shell Chemical L.P. The alpha olefin can be single chain length (C_{16} or C_{18}) or a mixture of different chain lengths (C_{16-18} or C_{20-24}). Generally, the alpha olefins (1-alkenes) are used "as is," wherein they are in a liquid phase.

It is, of course, also possible to isomerize more than one type of 1-alkene at the same time. For example, mixtures of two, three, four, five, six and more 1-alkenes can be employed. Moreover, it is not necessary that the 1-alkenes be employed in a substantially pure or purified form. Rather, they can be employed as a mixture (or contaminated) with one or more other compounds which are not 1-alkenes, provided said other compounds do not substantially interfere with the isomerization. Typical examples of other compounds which may (and often will) be present in the starting material are internal alkenes as well as saturated (cyclo)aliphatic and aromatic hydrocarbons.

The catalyst composition may comprise either potassium carbonate or potassium acetate.

The porous refractory oxide of the catalyst composition may be any refractory oxide material that has the properties suitable for use as the support component of the catalyst composition. Examples of possible suitable porous refractory oxide materials include magnesia, zirconia, titania, and alumina. The alumina may be of various forms, such as, alpha alumina, beta alumina, gamma alumina, delta alumina, eta alumina, theta alumina, boehmite, or mixtures thereof. The preferred porous refractory material is amorphous alumina. Among the available amorphous aluminas, gamma alumina is most preferred.

The porous refractory oxide generally may have an average pore diameter in the range of from 50 Angstroms to 160 Angstroms, preferably, from 70 Angstroms to 150 Angstroms, and, most preferably, from 80 Angstroms to 130 Angstroms. The total pore volume of the porous refractory oxide, as measured by standard mercury porisimetry methods, may be in the range of from 0.2 cc/gram to 2 cc/gram. Preferably, the pore volume may be in the range of from 0.3 cc/gram to 1.5 cc/gram, and, most preferably, from 0.4 cc/gram to 1 cc/gram. The surface area of the porous refractory oxide, as measured by the B.E.T. method, generally exceeds 100 m^2/gram, and it may typically be in the range of from 100 to 400 m^2/gram. As for the pore size distribution of the porous refractory oxide, at least of 70 percent of the total pore volume may be in the pores having diameters in the range of from 70 Angstroms to 150 Angstroms. More typically, at least 80 percent and even 90 percent of the total pore volume may be in the pores having diameters in the range of from 70 Angstroms to 150 Angstroms.

The amount of potassium carbonate or potassium acetate (catalyst) present in the catalyst composition may be 10 to 30 weight percent, preferably 15 to 20 weight percent, based

on potassium in the total catalyst composition. If less than 10 weight percent potassium is present in the catalyst, the activity will be too low. If more than 30 weight percent of the catalyst is used, it may plug the pores and make the catalyst composition ineffective.

The catalyst compositions of the present invention may be made, for example, by dissolving potassium carbonate or potassium acetate in water, such that the volume of solution exactly equals the pore volume of the porous refractory oxide material at a temperature up to 80°C. The solution may be cooled to below 40°C, and added to the porous refractory oxide material, using a regular pore volume impregnation technique. The wet catalyst may be aged for at least one hour, dried at elevated temperature, i.e., 175°C and calcined at standard calcining temperature, i.e., 480°C.

It is important that the catalyst be activated or else the isomerization reaction will occur very slowly or not occur at all. It is theorized that this step involves removing the last of the carbon dioxide and water from the catalyst so that all of the surface is available for catalytic activity.

The activation involves an oxygen-containing gas, preferably air, flowing through the catalyst composition at elevated temperature, follwed by an inert gas such as nitrogen, argon or helium, also at elevated temperature. It has been found that the activation flow rate (gas linear velocity) of both the oxygen-containing gas and the inert gas may be at least 250 cm/min in order for catalyst activation to take place. The temperature may be at least 350°C. The activation step preferably may last for from 2 to 24 hours, more preferably from 4 to 12 hours.

The preferred activation conditions are defined by the following formula

$$k(isom) = a + bT + cF > 0$$

wherein k(isom) is the isomerization rate constant, which preferably is at least 0.05 and more preferably 0.1 or more (units – cubic centimeters of olefin/cubic centimeters of catalyst·minute), T is the temperature in °C, F is the gas linear velocity in centimeters per minute, a is a constant with units of k(isom) and equals -0.12 for the potassium acetate catalyst and -0.21 for the potassium carbonate catalyst, b is a coefficient with units k(isom)/°C and equals 0.0004 for the potassium acetate catalyst and 0.0007 for the potassium carbonate catalyst, and c is a coefficient with units of k(isom)/ centimeters per minute and equals 0.00003 for the potassium acetate catalyst and 0.00002 for the potassium carbonate catalyst.

In a preferred embodiment, the activation temperature may range from 350 to 600°C. In a preferred embodiment, the activation gas linear velocity may range from 300 to 2000 centimeters per minute.

The next step involves contacting at least one alpha olefin with the activated catalyst composition. The process herein is a process for double bond isomerization in which the double bond of an alpha olefin is moved to an interior position within the olefin molecule. The reaction conditions for the process can vary broadly depending upon the particular alpha olefins being isomerized and the specific catalyst utilized. Reaction conditions include the time, temperature and pressure sufficient to produce double bond isomerization of the alpha olefin feed compounds.

The operating conditions are those which result in substantially no olefin cracking. By substantially no olefin cracking is meant very low yield loss; i.e., less than 10

weight percent, preferably less than 5 weight percent, and more preferably less than 2 weight percent, of the feed is cracked to products having fewer carbon atoms than the feed. Generally, the reaction temperatures may be in the range from 0 to 500°C, preferably from 50 to 500°C, and more preferably from 50 to 200°C. The reaction pressure is not critical and will depend upon the temperature, reactants and equipment employed. Typically, the pressure is in the range from atmospheric to 1000 kPa, preferably from atmospheric to 500 kPa. In a continuous process, the weight hourly space velocity (weight of olefin per weight of catalyst) may vary broadly but may be in the range from 0.1 to 20, preferably in the range from 1 to 10.

It is preferred that the isomerization reaction take place in the absence of any sulfates. A significant amount of sulfate in the reaction, for example, 0.5 wt % or more, may react with the potassium on the catalyst to form potassium sulfate which has no catalytic activity, thus basically killing the catalyst.

The process of the present invention may be able to produce an internal olefin product which contains less than 0.1 percent dimer. The process may also produce an internal olefin product wherein the alpha olefin content is less than 5 weight percent.

EXAMPLES

Example 1

An isomerization catalyst comprising 20 percent by weight potassium acetate on alumina (PAC-20) was made by impregnating AX300 gamma alumina extrudate with an aqueous solution of 20 percent by weight potassium acetate, based on

potassium. The water was boiled off and the impregnated catalyst was calcined at 482°C in a muffle oven under air.

50 grams of the catalyst was added to each of four cleaned fixed bed reactors. Denstone was used as inert material to fill empty reactor volume. Denstone is an inert material containing 69 percent silica, 26 percent alumina, 1 percent titanium dioxide, 1 percent iron oxide, 1 percent magnesium oxide, 1 percent potassium oxide and 1 percent sodium oxide. This inert material does not interfere with the isomerization reaction and it is normally used in laboratory experiments to fill the empty volume when smaller reactors are not available or suitable for the experiment. 10 grams of KL 5715 was loaded into each reactor as a guard bed to prolong the life of the catalyst. KL 5715 is an adsorbent catalyst which contains 10 percent copper oxide and 90 percent aluminum oxide. KL 5715 is used to remove phosphorus compounds present as impurities in the alpha olefin feeds. Such phosphorus compounds deactivate solid base catalysts.

The catalyst was activated by heating it at 450°C under a flow rate of air of 1000 cubic centimeters per minute for 4 hours, followed by 14.5 hours under flowing nitrogen at 1000 cubic centimeters per minute.

In the isomerization reaction, all reactors were run at 120°C and 35 kPa of pressure. The initial alpha olefin flow rate was 50 grams per hour (weight hourly space velocity of 1). Samples were taken for each reactor at reaction time 0 and samples were taken at various intervals during the reaction and submitted for percent isomerization analysis. The feed flow rate was adjusted and/or the reaction temperature was adjusted to maintain the percent isomerization in the range of 85-95 percent.

Each of the reactors was run until a total of 10 gallons of the isomerized internal olefins were obtained at 90 percent

isomerization. It was found that the conditions to give a product with 86 percent isomerization were a reaction temperature of 150°C and an olefin flow rate of 100 grams per hour(weight hourly space velocity of 2). The products from each reactor were combined and analyzed to give 10 gallons of product with 86 percent isomerization. The percent isomerization is a measure of how close the reaction has approached the equilibrium for the reaction. Therefore, 86 percent isomerization means that the reaction has gone 86 percent of the way to the equilibrium. The results of the four reactions are shown in the following Table 1.

Table 1

	Elapsed Time in Hours	Olefin Flow in grams/hour	Measured Percent Isomerization (for C_{16})	% Mole Alpha Olefin (for C_{16})
Reactor 5 at 150°C	46	93	86	2
	65	97	81	3
	89	94	76	4
Reactor 6 at 150°C	46	94	96	2
	65	97	94	2
	89	92	93	2
	116	101	87	2
	138	101	79	3
Reactor 7 at 150°C	65	49	93	2
	88	44	92	2
	114	47	91	2
	138	50	89	2
Reactor 8 at 150°C	44	79	94	2
	63	74	88	2
	86	76	80	3

Example 2

In this example, batch isomerization experiments were conducted to compare isomerization activity of a potassium carbonate on alumina (PCA-20) catalyst activated at different conditions. An isomerization catalyst comprising 20 percent by weight potassium carbonate on alumina (PCA-20) was made by

impregnating AX-202 alumina extrude with an aqueous solution of 20 percent potassium carbonate. Then water was boiled off. The impregnated catalyst was calcined at 482°C in a muffle oven under air.

50 grams of the catalyst were activated by heating in a tubular reactor at 550°C under airflow followed by argon flow. Various flows of argon and air were explored. Catalyst activation and reaction results are shown in Table 2. After activation, the catalyst was kept in an inert atmosphere to prevent deactivation due to moisture from air.

In the batch isomerization reaction, 100 grams of 1-hexadecene were isomerized using 3 grams of the activated PCA-20 catalyst. The reaction was run at 75°C and atmospheric pressure (101 kPa) for 90 minutes. Samples were taken at reaction times of 0, 30, 60 and 90 minutes and then were analyzed for percent isomerization. The isomerization rate constant, k(isom) for each reaction was calculated. Units of k(isom) are cubic centimeters of olefin/cubic centimeters of catalyst·minute (cc olefin/(cc catalyst·minute)). Samples were not analyzed for dimerized and branched olefins. These experiments were conducted to compare isomerization activity of PCA-20 catalyst activated under different conditions.

It was found that the second air treatment of the activation step (calcination being referred to as the first part) described above is not necessary if the catalyst has been properly manufactured. Argon only will suffice if the catalyst had previously been treated by calcining it in air at at least 350°C.

Table 2

Catalyst Activation Temperature	Activation Air Flow cm/minute	Activation Argon Flow cm/minute	Isomerization Rate Constant (cc olefin/cc catalyst·minute)
500°C	930 for 4 hours	93 for 12 hours	0.33
500°C	None	930 for 15 hours	0.32
500°C	930 for 15 hours	None	0.16

Example 3

A similar C_{16-18} internal olefin sample was prepared using the solid acid catalyst (X-600) used in the examples of U.S. Published Patent Application 2005/0070747, which is herein incorporated by reference in its entirety.

The X-600 solid acid catalyst was made by precipitating alumina in a silica slurry, followed by firing. The catalyst was prepared by reducing the pH of sodium silicate from its relatively high pH of over 11 to 3.0 by the addition of sulfuric acid. This results in the formation of a thick, pasty gel. Once the silica gel has been generated, the pH is adjusted upward to approximately 8.1 by the addition of sodium aluminate. Once the pH of 8.1 is reached, precipitation begins. At this point, both the aluminate and aluminum sulfate were added at a rate sufficient to maintain the pH at 8.1. Once all of the aluminum sulfate has been added, more aluminate was added to bring the pH up to approximately 10.3. The high pH is required in order that the sulfate may be washed out of the slurry. The material at this point is a thick slurry.

The sulfate and the sodium, introduced with the alumina precursors and sulfuric acid, were then washed out of the slurry by treatment of the slurry with deionized water. The washings occured in stages, with the first taking place at pH

10.3 (sulfate removal). For the second wash, the pH was decreased to approximately 6.0 to facilitate the removal of sodium. Finally, the pH was reduced to 3.7 to allow removal of the last traces of sodium. After this wash, the pH was increased to 5.0 by the addition of a strong base, such as ammonia. The pH must be raised to enable filtering of the slurry. After the washings were completed, the material was spray dried to yield, as a final powder, amorphous silica-alumina. The BET surface area of the catalyst was greater than 400 m^2/g with a total pore volume of 0.7 to 0.8 g/ml.

The X-600 solid acid catalyst was activated by heating it to 205°C with hot nitrogen flow for 24 hours.

The C_{16-18} internal olefin sample was prepared by flowing 3,700 lbs/hr (8140 kg/hr) C_{16-18} alpha olefin over a 2.5 foot X 10 foot (0.76 meter X 3.05 meter) reactor containing 1,000 lbs (2200 kg) of activated X-600 solid acid catalyst. The C_{16-18} alpha olefin had been dried over 13X molecular sieves, purified over AX-200 gamma alumina and pre-heated to 120°C prior to being fed to the isomerization reactor. The following Table 3 shows a comparison of the properties of the internal olefin samples made by the invention (from Example 1) and by the prior art acid catalyst.

Table 3: Comparison of C_{16-18} internal olefin samples prepared with PAC-20 and X-600 catalysts.

PROPERTY	METHOD	PAC-20	X-600
Carbon number, %w C16		58	56
Carbon number, %w C18		40	40
Branched C16, %w max		2	3
Branched C18, %w max		5	6
Isomerization, % min		86	55
n-Alpha Olefin, %w max		2	4
Dimer content, % as C28+, max		<0.05	7
Water, ppmw max	ASTM D-1744	26	61
Color, PtCo, max	ASTM D-1209	0	0
Appearance	Visual	Note 1	Note 1
Pour Point, °C	ASTM D-97	-12	-6
Flash Point, °C	ASTM D-3278	135	141
Kinematic Viscosity, cSt	ASTM D-445		
0(°C)		8.0	9.4
20(°C)		4.6	
25(°C)			4.7
40(°C)		3.0	3.4
100(°C)		1.3	1.4

(1) Clear & substantially free of visible impurities @ 20-25°C.

A comparison of the two samples shows that the sample prepared by the process of the present invention had less branching, a higher degree of isomerization, less alpha olefin, a lower dimer content, a lower pour point, and a lower kinematic viscosity.

C L A I M S

1. A process for producing internal olefins which comprises

(a) activating a catalyst composition comprising potassium carbonate or potassium acetate supported on a porous refractory oxide material, preferably amorphous gamma alumina, by heating it to a temperature of at least 350°C and causing an oxygen-containing gas, preferably air, to flow through the catalyst composition at a gas linear velocity of at least 250 centimeters per minute and then causing an inert gas, such as nitrogen, argon, or helium, to flow through the catalyst composition at a gas linear velocity of at least 250 centimeters per minute, and

(b) contacting at least one alpha olefin with the activated catalyst composition.

2. The process of claim 1 wherein a catalyst composition comprising potassium acetate supported on a porous refractory oxide material is activated under activation conditions of heat and gas flow defined by the formula

$$k(isom) = a + bT + cF > 0$$

wherein k(isom) is the isomerization rate constant (units - cubic centimeters of olefin/cubic centimeters of catalyst·minute), T is the temperature in °C, F is the gas linear velocity in cm/min, a is -0.12 cubic centimeters of olefin/cubic centimeters of catalyst·minute, b is 0.0004 (cubic centimeters of olefin/cubic centimeters of catalyst·minute)/°C, and c is a coefficient with units of cubic centimeters of olefin/cubic centimeters of

catalyst·minute) and is 0.00003 (cubic centimeters of olefin/cubic centimeters of catalyst·minute)/(cm/min).

3. The process of claims 1 or 2 wherein the activation temperature is from 350 to 600°C.

4. The process of claims 1 to 3 wherein the activation gas flow rate is from 300 to 2000 cubic centimeters per minute.

5. The process of claims 1 to 4 wherein the isomerization temperature is from 50 to 200°C.

6. The process of claim 1 to 5 wherein the isomerization pressure is from atmospheric to 1000 kPa.

7. The process of claims 1 to 6 wherein the process in step (b) is continuous and the alpha olefin weight hourly space velocity is from 0.1 to 20.

8. The process of claims 1 to 7 wherein the catalyst composition comprises from 10 to 30 weight percent of the potassium salt, based on potassium and the total weight of the catalyst composition.

9. The process of claims 1 to 8 wherein less than 0.5 percent by weight of sulfate is present in step (b).

10. The process of claims 1 to 9 wherein k(isom) is at least 0.05.

11. The process of claim 1 wherein a catalyst composition comprising potassium carbonate supported on a porous

refractory oxide material is activated under activation conditions of heat and gas flow defined by the formula

$$k(isom) = a + bT + cF > 0$$

wherein k(isom) is the isomerization rate constant (units - cubic centimeters of olefin/cubic centimeters of catalyst·minute), T is the temperature in °C, F is the gas linear velocity in cm/min, a is -0.21 cubic centimeters of olefin/cubic centimeters of catalyst·minute, b is 0.0007 (cubic centimeters of olefin/cubic centimeters of catalyst·minute)/°C, and c is a coefficient with units of cubic centimeters of olefin/cubic centimeters of catalyst·minute) and is 0.00002 (cubic centimeters of olefin/cubic centimeters of catalyst·minute)/(cm/min).

12. The process of claims 1 or 11 wherein the activation temperature is from 350 to 600°C.

13. The process of claims 1 and 11 or 12 wherein the activation gas flow rate is from 300 to 2000 cubic centimeters per minute.

14. The process of claims 1 and 11 to 13 wherein the isomerization temperature is from 50 to 200°C.

15. The process of claims 1 and 11 to 14 wherein the isomerization pressure is from atmospheric to 1000 kPa.

16. The process of claims 1 and 11 to 15 wherein the process in step (b) is continuous and the alpha olefin weight hourly space velocity is from 0.1 to 20.

17. The process of claims 1 and 11 to 16 wherein the catalyst composition comprises from 10 to 30 weight percent of the potassium salt, based on potassium and the total weight of the catalyst composition.

18. The process of claims 1 and 11 to 17 wherein less than 0.5 percent by weight of sulfate is present in step (b).

19. The process of claims 1 and 11 to 18 wherein k(isom) is at least 0.05.

20. An internal olefin product which is produced by double bond isomerization of an alpha olefin and which comprises less than 0.1 weight percent dimer.

21. The product of claim 20 wherein the alpha olefin content is less than 5 weight percent.

INTERNATIONAL SEARCH REPORT

International application No
PCT/US2008/058969

A. CLASSIFICATION OF SUBJECT MATTER
INV. C07C5/25 C07C11/02

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

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	GB 1 439 692 A (SHELL INT RESEARCH) 16 June 1976 (1976-06-16) page 2, left-hand column, line 34 - line 36 pages 3,6 claims table I examples	1-21
X	EP 0 370 553 A (SHELL INT RESEARCH [NL]) 30 May 1990 (1990-05-30) page 112; table 5	20,21
A	the whole document	1-19
X	WO 00/03961 A (CHEVRON CHEM CO [US]) 27 January 2000 (2000-01-27) examples	20,21
A	the whole document	1-19

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[X] Further documents are listed in the continuation of Box C.

[X] See patent family annex.

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Date of the actual completion of the international search	Date of mailing of the international search report
3 September 2008	17/09/2008

Name and mailing address of the ISA/	Authorized officer
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INTERNATIONAL SEARCH REPORT

International application No
PCT/US2008/058969

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 2005/070747 A1 (BROWN DAVID STEPHEN [US] ET AL) 31 March 2005 (2005-03-31) cited in the application examples	20,21
A	the whole document	1-19

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No
PCT/US2008/058969

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
GB 1439692 A	16-06-1976	DE 2336138 A1	31-01-1974
		FR 2192992 A1	15-02-1974
		NL 7209849 A	25-10-1972
EP 0370553 A	30-05-1990	AU 623945 B2	28-05-1992
		AU 4537989 A	31-05-1990
		BR 8905914 A	19-06-1990
		CA 2003562 A1	23-05-1990
		CN 1043096 A	20-06-1990
		JP 2172813 A	04-07-1990
		ZA 8908864 A	29-08-1990
WO 0003961 A	27-01-2000	AU 762734 B2	03-07-2003
		AU 3879999 A	07-02-2000
		CA 2335085 A1	27-01-2000
		CN 1307552 A	08-08-2001
		CZ 20010134 A3	17-10-2001
		DE 69916841 D1	03-06-2004
		DE 69916841 T2	21-04-2005
		EP 1097119 A1	09-05-2001
		JP 2002520378 T	09-07-2002
		NO 20010204 A	12-01-2001
		RU 2203877 C2	10-05-2003
		US 6054629 A	25-04-2000
		ZA 200006839 A	05-06-2001
US 2005070747 A1	31-03-2005	NONE	