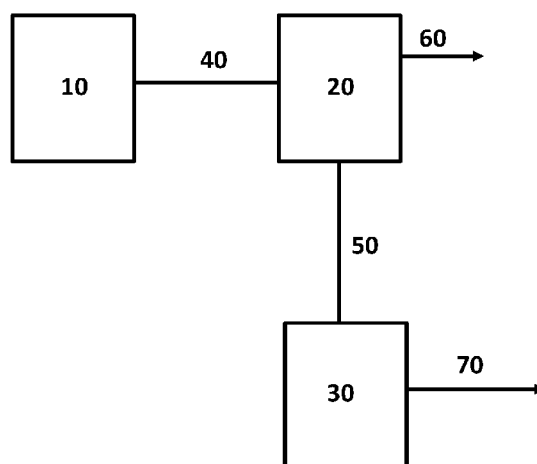




- (51) **International Patent Classification:**
C07C 1/20 (2006.01) *C07C 7/04* (2006.01)
C07C 1/22 (2006.01)
- (21) **International Application Number:**
PCT/US2015/067569
- (22) **International Filing Date:**
28 December 2015 (28.12.2015)
- (25) **Filing Language:** English
- (26) **Publication Language:** English
- (30) **Priority Data:**
14200564.4 30 December 2014 (30.12.2014) EP
- (71) **Applicant (for US only):** SHELL OIL COMPANY
[US/US]; One Shell Plaza, P.O. Box 2463, Houston, Texas
77252-2463 (US).
- (71) **Applicant (for all designated States except US):** SHELL
INTERNATIONALE RESEARCH MAATSCHAPPIJ
B.V. [NL/NL]; Carel van Bylandtlaan 30, NL-2596 The
Hague (NL).
- (72) **Inventors:** MARSMAN, Jeroen Gerard; Grasweg 31,
1031 HW Amsterdam (NL). CHEWTER, Leslie Andrew;
Grasweg 31, 1031 HW Amsterdam (NL).
- (74) **Agent:** CARRUTH, James D.; Shell Oil Company, One
Shell Plaza, P.O. Box 2463, Houston, Texas 77252-2463
(US).
- (81) **Designated States** (unless otherwise indicated, for every
kind of national protection available): AE, AG, AL, AM,
AO, AT, AU, AZ, BA, BB, BG, BH, BN, BR, BW, BY,
BZ, CA, CH, CL, CN, CO, CR, CU, CZ, DE, DK, DM,
DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT,
HN, HR, HU, ID, IL, IN, IR, IS, JP, KE, KG, KN, KP, KR,
KZ, LA, LC, LK, LR, LS, LU, LY, MA, MD, ME, MG,
MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM,
PA, PE, PG, PH, PL, PT, QA, RO, RS, RU, RW, SA, SC,
SD, SE, SG, SK, SL, SM, ST, SV, SY, TH, TJ, TM, TN,
TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.
- (84) **Designated States** (unless otherwise indicated, for every
kind of regional protection available): ARIPO (BW, GH,
GM, KE, LR, LS, MW, MZ, NA, RW, SD, SL, ST, SZ,
TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, RU,
TJ, TM), European (AL, AT, BE, BG, CH, CY, CZ, DE,
DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU,
LV, MC, MK, MT, NL, NO, PL, PT, RO, RS, SE, SI, SK,
SM, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ,
GW, KM, ML, MR, NE, SN, TD, TG).
- Published:**
— with international search report (Art. 21(3))

(54) **Title:** AN OXYGENATE CONVERSION PROCESS

FIG. 1



(57) **Abstract:** A process for converting oxygenates into alkylate comprising: a) feeding an oxygenate containing feed to an oxygenate to olefins conversion reactor; b) contacting the oxygenate containing feed with a molecular sieve catalyst under oxygenate to olefins conversion conditions in the reactor to form a product stream comprising propylene, ethylene and mixed C4s; c) separating the mixed C4s from the product stream to form a mixed C4 stream; d) passing at least a fraction of the mixed C4 stream to an alkylation process to produce alkylate.

AN OXYGENATE CONVERSION PROCESS

Reference to Related Applications

The present application claims the benefit of European Patent Application Serial No. 14200564.4, filed on 30 December 2014.

5 Field of the Invention

The invention relates to a process for converting oxygenates to alkylate.

Background of the Invention

Oxygenate-to-olefin processes are well described in the art. Typically, oxygenate-to-olefin processes are used to produce predominantly ethylene and propylene. An example
10 of such an oxygenate-to-olefin process is described in US Patent Application Publication No. 2011/112344, which is herein incorporated by reference. The publication describes a process for the preparation of an olefin product comprising ethylene and/or propylene, comprising a step of converting an oxygenate feedstock in an oxygenate-to-olefins conversion system, comprising a reaction zone in which an oxygenate feedstock is
15 contacted with an oxygenate conversion catalyst under oxygenate conversion conditions, to obtain a conversion effluent comprising ethylene and/or propylene.

Additional compounds, especially higher molecular weight hydrocarbons are typically produced with the ethylene and propylene in an oxygenate-to-olefins process. A method of improving the yield of lower molecular weight olefins is desired as these
20 olefins, mainly ethylene and propylene, serve as feeds for the production of numerous chemicals. The catalyst and the activity of the catalyst is key to the performance of the reaction step.

Summary of the Invention

The invention provides a process for converting oxygenates into alkylate
25 comprising: a) feeding an oxygenate containing feed to an oxygenate to olefins conversion reactor; b) contacting the oxygenate containing feed with a molecular sieve catalyst under oxygenate to olefins conversion conditions in the reactor to form a product stream comprising propylene, ethylene and mixed C4s; c) separating the mixed C4s from the product stream to form a mixed C4 stream; d) passing at least a portion of the mixed C4
30 stream to an alkylation process to produce alkylate.

Brief Description of the Drawings

Figure 1 depicts an embodiment of the process.

_ propylene and/or ethylene. This improved process of integrating the oxygenate to olefins conversion reaction with an alkylation unit removes the need for such an additional reactor
5 if the entire mixed C4 stream is alkylated. If only a portion of the mixed C4 stream were alkylated then this would reduce the size of such an olefin cracking reactor. Further, this process provides feeds for an alkylation unit which produces a high octane motor gasoline blending component.

The oxygenate to olefins process receives as a feedstock a stream comprising one
10 or more oxygenates. An oxygenate is an organic compound that contains at least one oxygen atom. The oxygenate is preferably one or more alcohols, preferably aliphatic alcohols where the aliphatic moiety has from 1 to 20 carbon atoms, preferably from 1 to 10 carbon atoms, more preferably from 1 to 5 carbon atoms and most preferably from 1 to 4 carbon atoms. The alcohols that can be used as a feed to this process include lower straight
15 and branched chain aliphatic alcohols. In addition, ethers and other oxygen containing organic molecules can be used. Suitable examples of oxygenates include methanol, ethanol, n-propanol, isopropanol, methyl ethyl ether, dimethyl ether, diethyl ether, di-isopropyl ether, formaldehyde, dimethyl carbonate, dimethyl ketone, acetic acid and mixtures thereof. In a preferred embodiment, the feedstock comprises one or more of
20 methanol, ethanol, dimethyl ether, diethyl ether or a combination thereof, more preferably methanol or dimethyl ether and most preferably methanol.

In one embodiment, the oxygenate is obtained as a reaction product of synthesis gas. Synthesis gas can, for example, be generated from fossil fuels, such as from natural gas or oil, or from the gasification of coal. In another embodiment, the oxygenate is
25 obtained from biomaterials, such as through fermentation.

The oxygenate feedstock can be obtained from a pre-reactor, which converts methanol at least partially into dimethylether and water. Water may be removed, by e.g., distillation. In this way, less water is present in the process of converting oxygenates to olefins, which has advantages for the process design and lowers the severity of
30 hydrothermal conditions to which the catalyst is exposed.

The oxygenate to olefins process, may in certain embodiments, also receive an olefin co-feed. This co-feed may comprise olefins having carbon numbers of from 1 to 8,

preferably from 3 to 6 and more preferably 4 or 5. Examples of suitable olefin co-feeds include butene, pentene and hexene.

Preferably, the oxygenate feed comprises one or more oxygenates and olefins, more preferably oxygenates and olefins in an oxygenate:olefin molar ratio in the range of from 5 1000:1 to 1:1, preferably 100:1 to 1:1. More preferably, in a oxygenate:olefin molar ratio in the range of from 20:1 to 1:1, more preferably in the range of 18:1 to 1:1, still more preferably in the range of 15:1 to 1:1, even still more preferably in the range of 14:1 to 1:1. It is preferred to convert a C4 olefin, recycled from the oxygenate to olefins conversion reaction together with an oxygenate, to obtain a high yield of ethylene and propylene, 10 therefore preferably at least one mole of oxygenate is provided for every mole of C4 olefin.

The olefin co-feed may also comprise paraffins. These paraffins may serve as diluents or in some cases they may participate in one or more of the reactions taking place in the presence of the catalyst. The paraffins may include alkanes having carbon numbers from 1 to 10, preferably from 3 to 6 and more preferably 4 or 5. The paraffins may be 15 recycled from separation steps occurring downstream of the oxygenate to olefins conversion step.

The oxygenate to olefins process, may in certain embodiments, also receive a diluent co-feed to reduce the concentration of the oxygenates in the feed and suppress side reactions that lead primarily to high molecular weight products. The diluent should 20 generally be non-reactive to the oxygenate feedstock or to the catalyst. Possible diluents include helium, argon, nitrogen, carbon monoxide, carbon dioxide, methane, water and mixtures thereof. The more preferred diluents are water and nitrogen with the most preferred being water.

The diluent may be used in either liquid or vapor form. The diluent may be added 25 to the feedstock before or at the time of entering the reactor or added separately to the reactor or added with the catalyst. In one embodiment, the diluents is added in an amount in the range of from 1 to 90 mole percent, more preferably from 1 to 80 mole percent, more preferably from 5 to 50 mole percent, most preferably from 5 to 40 mole percent.

During the conversion of the oxygenates in the oxygenate to olefins conversion 30 reactor, steam is produced as a by-product, which serves as an in-situ produced diluent. Typically, additional steam is added as diluent. The amount of additional diluent that needs to be added depends on the in-situ water make, which in turn depends on the composition

of the oxygenate feed. Where the diluent provided to the reactor is water or steam, the molar ratio of oxygenate to diluent is between 10:1 and 1:20.

The oxygenate feed is contacted with the catalyst at a temperature in the range of from 200 to 1000 °C, preferably of from 300 to 800 °C, more preferably of from 350 to 700 °C, even more preferably of from 450 to 650°C. The feed may be contacted with the catalyst at a temperature in the range of from 530 to 620 °C, or preferably of from 580 to 610 °C. The feed may be contacted with the catalyst at a pressure in the range of from 0.1 kPa (1 mbar) to 5 MPa (50 bar), preferably of from 100 kPa (1 bar) to 1.5 MPa (15 bar), more preferably of from 100 kPa (1 bar) to 300 kPa (3 bar). Reference herein to pressures is to absolute pressures.

A wide range of WHSV for the feedstock may be used. WHSV is defined as the mass of the feed (excluding diluents) per hour per mass of catalyst. The WHSV should preferably be in the range of from 1 hr⁻¹ to 5000 hr⁻¹.

The process takes place in a reactor and the catalyst may be present in the form of a fixed bed, a moving bed, a fluidized bed, a dense fluidized bed, a fast or turbulent fluidized bed, a circulating fluidized bed. In addition, riser reactors, hybrid reactors or other reactor types known to those skilled in the art may be used. In another embodiment, more than one of these reactor types may be used in series. In one embodiment, the reactor is a riser reactor. The advantage of a riser reactor is that it allows for very accurate control of the contact time of the feed with the catalyst, as riser reactors exhibit a flow of catalyst and reactants through the reactor that approaches plug flow.

The feedstocks described above are converted primarily into olefins. The olefins produced from the feedstock typically have from 2 to 30 carbon atoms, preferably from 2 to 8 carbon atoms, more preferably from 2 to 6 carbon atoms, most preferably ethylene and/or propylene. In addition to these olefins, diolefins having from 4 to 18 carbon atoms, conjugated or nonconjugated dienes, polyenes, vinyl monomers and cyclic olefins may be produced in the reaction.

In a preferred embodiment, the feedstock, preferably one or more oxygenates, is converted in the presence of a molecular sieve catalyst into olefins having from 2 to 6 carbon atoms. Preferably the oxygenate is methanol, and the olefins are ethylene and/or propylene.

The products from the reactor are typically separated and/or purified to prepare separate product streams in a recovery system. Such systems typically comprise one or

more separation, fractionation or distillation towers, columns, and splitters and other associated equipment, for example, various condensers, heat exchangers, refrigeration systems or chill trains, compressors, knock-out drums or pots, pumps and the like.

The recovery system may include a demethanizer, a deethanizer, a depropanizer, a wash tower often referred to as a caustic wash tower and/or quench tower, absorbers, adsorbers, membranes, an ethylene-ethane splitter, a propylene-propane splitter, a and the like.

Typically in the recovery system, additional products, by-products and/or contaminants may be formed along with the preferred olefin products. The preferred products, ethylene and propylene are preferably separated and purified for use in derivative processes such as polymerization processes.

In addition to the propylene and ethylene, the products may comprise C4+ olefins, paraffins and aromatics that may be further reacted, recycled or otherwise further treated to increase the yield of the desired products and/or other valuable products. C4+ olefins may be recycled to the oxygenate to olefins conversion reaction or fed to a separate reactor for cracking. The paraffins may also be cracked in a separate reactor, and/or removed from the system to be used elsewhere or possibly as fuel.

Although less desired, the product will typically comprise some aromatic compounds such as benzene, toluene and xylenes.

The mixed C4 stream or at least a portion of it can be fed to an alkylation unit to form alkylate, which is a very valuable component of motor gasoline. Alkylate is typically iso-octane but can also be iso-heptane. Before the mixed C4 stream is fed to an alkylation unit, it can be passed through an etherification step where the isobutylenes present react with methanol to form MTBE which is then removed from the C4 stream.

In one embodiment, the mixed C4 stream is passed to a direct alkylation unit. A direct alkylation unit uses an acid, sulfuric or hydrofluoric, to convert the C4s to alkylate.

In another embodiment, the mixed C4 stream is passed to an indirect alkylation unit. In this process the isobutylenes in the mixed C4 stream are dimerized by passing them over an acidic resin or a solid phosphoric acid to form alkylate. In this process, there is a remaining mixed C4 stream, and this stream can be recycled to the oxygenate conversion step or passed to a direct alkylation unit.

Figure 1 depicts an embodiment of the invention. The oxygenate conversion system 10 receives an oxygenate containing feed. The feed is contacted with an oxygenate

conversion catalyst and the product stream 40 is passed to a separation step 20. The ethylene 60 is separated from the products. A mixed C4 stream 50 is also separated from the product stream and is passed to an alkylation step 30. The mixed C4s are converted to alkylate 70. Additional isobutane may also be fed to the alkylation unit. In addition, other products may be separated in the separation step 20.

The C4+ olefins and paraffins formed in the oxygenate to olefins conversion reactor may be further reacted in an additional reactor containing the same or a different molecular sieve catalyst. In this additional reactor, the C4+ feed is converted over the molecular sieve catalyst at a temperature in the range of from 500 to 700 °C. The additional reactor is also referred to as an OCP reactor and the process that takes place in this reactor is referred to as an olefin cracking process. In contact with the molecular sieve catalyst, at least part of the olefins in the C4+ feed is converted to a product, which includes at least ethylene and/or propylene and preferably both. In addition to ethylene and/or propylene, the gaseous product may comprise higher olefins, i.e. C4+ olefins, and paraffins. The gaseous product is retrieved from the second reactor as part of a second reactor effluent stream.

The olefin feed is contacted with the catalyst at a temperature in the range of from 500 to 700 °C, preferably of from 550 to 650°C, more preferably of from 550 to 620°C, even more preferably of from 580 to 610°C; and a pressure in the range of from 0.1 kPa (1 mbara) to 5 MPa (50 bara), preferably of from 100 kPa (1 bara) to 1.5 MPa (15 bara), more preferably of from 100 kPa (1 bara) to 300 kPa (3 bara). Reference herein to pressures is to absolute pressures.

In one embodiment, the C4+ olefins are separated into at least two fractions: a C4 olefin fraction and a C5+ olefin fraction. In this embodiment, the C4 olefins are recycled to the oxygenate to olefins conversion reactor and the C5+ olefins are fed to the OCP reactor. The cracking behavior of C4 olefins and C5 olefins is believed to be different when contacted with a molecular sieve catalyst, in particular above 500 °C.

The cracking of C4 olefins is an indirect process which involves a primary oligomerisation process to a C8, C12 or higher olefin followed by cracking of the oligomers to lower molecular weight hydrocarbons including ethylene and propylene, but also, amongst other things, to C5 to C7 olefins, and by-products such as C2 to C6 paraffins, cyclic hydrocarbons and aromatics. In addition, the cracking of C4 olefins is prone to coke formation, which places a restriction on the obtainable conversion of the C4

olefins. Generally, paraffins, cyclics and aromatics are not formed by cracking. They are formed by hydrogen transfer reactions and cyclisation reactions. This is more likely in larger molecules. Hence the C4 olefin cracking process, which as mentioned above includes intermediate oligomerisation, is more prone to by-product formation than direct
5 cracking of C5 olefins. The conversion of the C4 olefins is typically a function of the temperature and space time (often expressed as the weight hourly space velocity). With increasing temperature and decreasing weight hourly space velocity (WHSV) conversion of the C4 olefins in the feed to the OCP increases. Initially, the ethylene and propylene yields increase, but, at higher conversions, yield decreases at the cost of a higher by-
10 product make and, in particular, a higher coke make, limiting significantly the maximum yield obtainable.

Contrary to C4 olefins, C5 olefin cracking is ideally a relatively straight forward-process whereby the C5 olefin cracks into a C2 and a C3 olefin, in particular above 500°C. This cracking reaction can be run at high conversions, up to 100%, while maintaining, at
15 least compared to C4 olefins, high ethylene and propylene yields with a significantly lower by-product and coke make. Although, C5+ olefins can also oligomerise, this process competes with the more beneficial cracking to ethylene and propylene.

In a preferred embodiment of the process according to the present invention, instead of cracking the C4 olefins in the OCP reactor, the C4 olefins are recycled to the
20 oxygenate to olefins conversion reactor. Again without wishing to be bound by any particular theory, it is believed that in the oxygenate to olefins conversion reactor the C4 olefins are alkylated with, for instance, methanol to C5 and/or C6 olefins. These C5 and/or C6 olefins may subsequently be converted into at least ethylene and/or propylene. The main by-products from this oxygenate to olefins conversion reaction are again C4 and C5
25 olefins, which can be recycled to the oxygenate to olefins conversion reactor and olefin cracking reactor, respectively.

Therefore, preferably, where the gaseous products further include C4 olefins, at least part of the C4 olefins are provided to (i) the oxygenate to olefins conversion reactor together with or as part of the oxygenate feed, and/or (ii) the olefin cracking reactor as part
30 of the olefin feed, more preferably at least part of the C4 olefins is provided to the oxygenate to olefins conversion reactor together with or as part of the oxygenate feed.

Preferably, where the gaseous products further include C5 olefins, at least part of the C5 olefins are provided to the olefin cracking reactor as part of the olefin feed.

Preferably, the olefin feed to the olefin cracking reactor comprises C4+ olefins, preferably C5+ olefins, more preferably C5 olefins.

In a preferred embodiment, the oxygenate to olefins conversion reactor and the optional OCP reactor are operated as riser reactors where the catalyst and feedstock are fed
5 at the base of the riser and an effluent stream with entrained catalyst exits the top of the riser. In this embodiment, gas/solid separators are necessary to separate the entrained catalyst from the reactor effluent. The gas/solid separator may be any separator suitable for separating gases from solids. Preferably, the gas/solid separator comprises one or more centrifugal separation units, preferably cyclone units, optionally combined with a stripper
10 section.

The reactor effluent is preferably cooled in the gas/solid separator to terminate the conversion process and prevent the formation of by-products outside the reactors. The cooling may be achieved by use of a water quench.

Once the catalyst is separated from the effluent, the catalyst may be returned to the
15 reaction zone from which it came, to another reaction zone or to a regeneration zone. Further, the catalyst that has been separated in the gas/solid separator may be combined with catalyst from other gas/solid separators before it is sent to a reaction zone or to the regeneration zone.

During conversion of the oxygenates to olefins, carbonaceous deposits known as
20 "coke" are formed on the surface of and/or within the molecular sieve catalysts. To avoid a significant reduction in activity of the catalyst, the catalyst must be regenerated by burning off the coke deposits.

In one embodiment, a portion of the coked molecular sieve catalyst is withdrawn from the reactor and introduced into a regeneration system. The regeneration system
25 comprises a regenerator where the coked catalyst is contacted with a regeneration medium, preferably an oxygen-containing gas, under regeneration temperature, pressure and residence time conditions.

Examples of suitable regeneration media include oxygen, O₃, SO₃, N₂O, NO, NO₂, N₂O₅, air, air enriched with oxygen, air diluted with nitrogen or carbon dioxide, oxygen
30 and water, carbon monoxide and/or hydrogen. The regeneration conditions are those capable of burning at least a portion of the coke from the coked catalyst, preferably to a coke level of less than 75% of the coke level on the catalyst entering the regenerator. More preferably the coke level is reduced to less than 50% of the coke level on the catalyst

entering the regenerator and most preferably the coke level is reduced to less than 30% of the coke level on the catalyst entering the regenerator. Complete removal of the coke is not necessary as this may result in degradation of the catalyst.

The regeneration temperature is in the range of from 200 °C to 1500 °C, preferably
5 from 300 °C to 1000 °C, more preferably from 450 °C to 700 °C and most preferably from 500 °C to 700 °C. In a preferred embodiment, the catalyst is regenerated at a temperature in the range of from 550 to 650 °C.

The preferred residence time of the coked molecular sieve catalyst in the regenerator is in the range of from 1 minute to several hours, most preferably 1 minute to
10 100 minutes. The preferred volume of oxygen in the regeneration medium is from 0.01 mole percent to 10 mole percent based on the total volume of the regeneration medium.

In one embodiment, regeneration promoters, typically metal containing compounds such as platinum and palladium are added to the regenerator directly or indirectly, for example with the coked catalyst composition. In another embodiment, a fresh molecular
15 sieve catalyst is added to the regenerator.

In an embodiment, a portion of the regenerated molecular sieve catalyst from the regenerator is returned to the reactor, directly to the reaction zone or indirectly by pre-contacting with the feedstock.

The burning of coke is an exothermic reaction and in certain embodiments, the
20 temperature in the regeneration system is controlled to prevent it from rising too high. Various known techniques for cooling the system and/or the regenerated catalyst may be employed including feeding a cooled gas to the regenerator, or passing the regenerated catalyst through a catalyst cooler. A portion of the cooled regenerated catalyst may be returned to the regenerator while another portion is returned to the reactor.

25 In certain embodiments, there is not sufficient coke on the catalyst to raise the temperature of the catalyst to desired levels. In one embodiment, a liquid or gaseous fuel may be fed to the regenerator where it will combust and provide additional heat to the catalyst.

Catalysts suitable for use in the conversion of oxygenates to olefins may be made
30 from practically any small or medium pore molecular sieve. One example of a suitable type of molecular sieve is a zeolite. Suitable zeolites include, but are not limited to AEI, AEL, AFT, AFO, APC, ATN, ATT, ATV, AWW, BIK, CAS, CHA, CHI, DAC, DDR, EDI, ERI, EUO, FER, GOO, HEU, KFI, LEV, LOV, LTA, MFI, MEL, MON, MTT, MTW,

PAU, PHI, RHO, ROG, THO, TON and substituted forms of these types. Suitable catalysts include those containing a zeolite of the ZSM group, in particular of the MFI type, such as ZSM-5, the MTT type, such as ZSM-23, the TON type, such as ZSM-22, the MEL type, such as ZSM-11, and the FER type. Other suitable zeolites are for example
5 zeolites of the STF-type, such as SSZ-35, the SFF type, such as SSZ-44 and the EU-2 type, such as ZSM-48. Preferred zeolites for this process include ZSM-5, ZSM-22 and ZSM-23.

A suitable molecular sieve catalyst may have a silica-to-alumina ratio (SAR) of less than 280, preferably less than 200 and more preferably less than 100. The SAR may be in the range of from 10 to 280, preferably from 15 to 200 and more preferably from 20 to
10 100.

A preferred MFI-type zeolite for the oxygenate to olefins conversion catalyst has a silica-to-alumina ratio, SAR, of at least 60, preferably at least 80. More preferred MFI-type zeolite has a silica-to-alumina ratio, SAR, in the range of 60 to 150, preferably in the range of 80 to 100.

15 The zeolite-comprising catalyst may comprise more than one zeolite. In that case it is preferred that the catalyst comprises at least a more-dimensional zeolite, in particular of the MFI type, more in particular ZSM-5, or of the MEL type, such as zeolite ZSM-11, and a one-dimensional zeolite having 10-membered ring channels, such as of the MTT and/or TON type.

20 It is preferred that zeolites in the hydrogen form are used in the zeolite-comprising catalyst, e.g., HZSM-5, HZSM-11, and HZSM-22, HZSM-23. Preferably at least 50wt%, more preferably at least 90wt%, still more preferably at least 95wt% and most preferably 100wt% of the total amount of zeolite used is in the hydrogen form. It is well known in the art how to produce such zeolites in the hydrogen form.

25 Another example of suitable molecular sieves are siliocoaluminophosphates (SAPOs). SAPOs have a three dimensional microporous crystal framework of PO_2^+ , AlO_2^- , and SiO_2 tetrahedral units. Suitable SAPOs include SAPO-17, -18, 34, -35, -44, but also SAPO-5, -8, -11, -20, -31, -36, 37, -40, -41, -42, -47 and -56; aluminophosphates (AlPO) and metal substituted (silico)aluminophosphates (MeAlPO), wherein the Me in
30 MeAlPO refers to a substituted metal atom, including metal selected from one of Group IA, IIA, IB, IIIB, IVB, VB, VIB, VIIB, VIIIB and lanthanides of the Periodic Table of Elements. Preferred SAPOs for this process include SAPO-34, SAPO-17 and SAPO-18.

Preferred substituent metals for the MeAlPO include Co, Cr, Cu, Fe, Ga, Ge, Mg, Mn, Ni, Sn, Ti, Zn and Zr.

The molecular sieves described above are formulated into molecular sieve catalyst compositions for use in the oxygenates to olefins conversion reaction and the olefin cracking step. The molecular sieves are formulated into catalysts by combining the molecular sieve with a binder and/or matrix material and/or filler and forming the composition into particles by techniques such as spray-drying, pelletizing, or extrusion. The molecular sieve may be further processed before being combined with the binder and/or matrix. For example, the molecular sieve may be milled and/or calcined.

Suitable binders for use in these molecular sieve catalyst compositions include various types of aluminas, aluminophosphates, silicas and/or other inorganic oxide sol. The binder acts like glue binding the molecular sieves and other materials together, particularly after thermal treatment. Various compounds may be added to stabilize the binder to allow processing.

Matrix materials are usually effective at among other benefits, increasing the density of the catalyst composition and increasing catalyst strength (crush strength and/or attrition resistance). Suitable matrix materials include one or more of the following: rare earth metals, metal oxides including titania, zirconia, magnesia, thoria, beryllia, quartz, silica or sols, and mixtures thereof, for example, silica-magnesia, silica-zirconia, silica-titania, and silica-alumina. In one embodiment, matrix materials are natural clays, for example, kaolin. A preferred matrix material is kaolin.

In one embodiment, the molecular sieve, binder and matrix material are combined in the presence of a liquid to form a molecular sieve catalyst slurry. The amount of binder is in the range of from 2 to 40 wt%, preferably in the range of from 10 to 35 wt%, more preferably in the range of from 15 to 30 wt%, based on the total weight of the molecular sieve, binder and matrix material, excluding liquid (after calcination).

After forming the slurry, the slurry may be mixed, preferably with rigorous mixing to form a substantially homogeneous mixture. Suitable liquids include one or more of water, alcohols, ketones, aldehydes and/or esters. Water is the preferred liquid. In one embodiment, the mixture is colloid-milled for a period of time sufficient to produce the desired texture, particle size or particle size distribution.

The molecular sieve, matrix and optional binder can be in the same or different liquids and are combined in any order together, simultaneously, sequentially or a combination thereof. In a preferred embodiment, water is the only liquid used.

In a preferred embodiment, the slurry is mixed or milled to achieve a uniform slurry
5 of sub-particles that is then fed to a forming unit. A slurry of the zeolite may be prepared and then milled before combining with the binder and/or matrix. In a preferred embodiment, the forming unit is a spray dryer. The forming unit is typically operated at a temperature high enough to remove most of the liquid from the slurry and from the resulting molecular sieve catalyst composition. In a preferred embodiment, the particles are
10 then exposed to ion-exchange using an ammonium nitrate or other appropriate solution.

In one embodiment, the ion exchange is carried out before the phosphorous impregnation. The ammonium nitrate is used to ion exchange the zeolite to remove alkali ions. The zeolite can be impregnated with phosphorous using phosphoric acid followed by a thermal treatment to H⁺ form. In another embodiment, the ion exchange is carried out
15 after the phosphorous impregnation. In this embodiment, alkali phosphates or phosphoric acid may be used to impregnate the zeolite with phosphorous, and then the ammonium nitrate and heat treatment are used to ion exchange and convert the zeolite to the H⁺ form.

Alternatively to spray drying the catalyst may be formed into spheres, tablets, rings, extrudates or any other shape known to one of ordinary skill in the art. The catalyst may
20 be extruded into various shapes, including cylinders and trilobes.

The average particle size is in the range of from 1-200 μm , preferably from 50-100 μm . If extrudates are formed, then the average size is in the range of from 1 mm to 10 mm, preferably from 2 mm to 7 mm.

The catalyst may further comprise phosphorus as such or in a compound, i.e.
25 phosphorus other than any phosphorus included in the framework of the molecular sieve. It is preferred that a MEL or MFI-type zeolite comprising catalyst additionally comprises phosphorus.

The molecular sieve catalyst is prepared by first forming a molecular sieve catalyst precursor as described above, optionally impregnating the catalyst with a phosphorous
30 containing compound and then calcining the catalyst precursor to form the catalyst. The phosphorous impregnation may be carried out by any method known to one of skill in the art.

The phosphorus-containing compound preferably comprises a phosphorus species such as PO_4^{3-} , $\text{P}(\text{OCH}_3)_3$, or P_2O_5 , especially PO_4^{3-} . Preferably the phosphorus-containing compound comprises a compound selected from the group consisting of ammonium phosphate, ammonium dihydrogen phosphate, dimethylphosphate, metaphosphoric acid
5 and trimethyl phosphite and phosphoric acid, especially phosphoric acid. The phosphorus containing compound is preferably not a Group II metal phosphate. Group II metal species include magnesium, calcium, strontium and barium; especially calcium.

In one embodiment, phosphorus can be deposited on the catalyst by impregnation using acidic solutions containing phosphoric acid (H_3PO_4). The concentration of the
10 solution can be adjusted to impregnate the desired amount of phosphorus on the precursor. The catalyst precursor may then be dried.

The catalyst precursor, containing phosphorous (either in the framework or impregnated) is calcined to form the catalyst. The calcination of the catalyst is important to determining the performance of the catalyst in the oxygenate to olefins process.
15 The calcination may be carried out in any type of calciner known to one of ordinary skill in the art. The calcination may be carried out in a tray calciner, a rotary calciner, or a batch oven optionally in the presence of an inert gas and/or oxygen and/or steam

The calcination may be carried out at a temperature in the range of from 400 °C to 1000 °C, preferably in a range of from 450 °C to 800 °C, more preferably in a range of
20 from 500 °C to 700 °C. Calcination time is typically dependent on the degree of hardening of the molecular sieve catalyst composition and the temperature and ranges from about 15 minutes to about 2 hours.

The calcination temperatures described above are temperatures that are reached for at least a portion of the calcination time. For example, in a rotary calciner, there may be
25 separate temperature zones that the catalyst passes through. For example, the first zone may be at a temperature in the range of from 100 to 300 °C. At least one of the zones is at the temperatures specified above. In a stationary calciner, the temperature is increased from ambient to the calcination temperatures above and so the temperature is not at the calcination temperature for the entire time.

In a preferred embodiment, the calcination is carried out in air at a temperature of
30 from 500 °C to 600 °C. The calcination is carried out for a period of time from 30 minutes to 15 hours, preferably from 1 hour to 10 hours, more preferably from 1 hour to 5 hours.

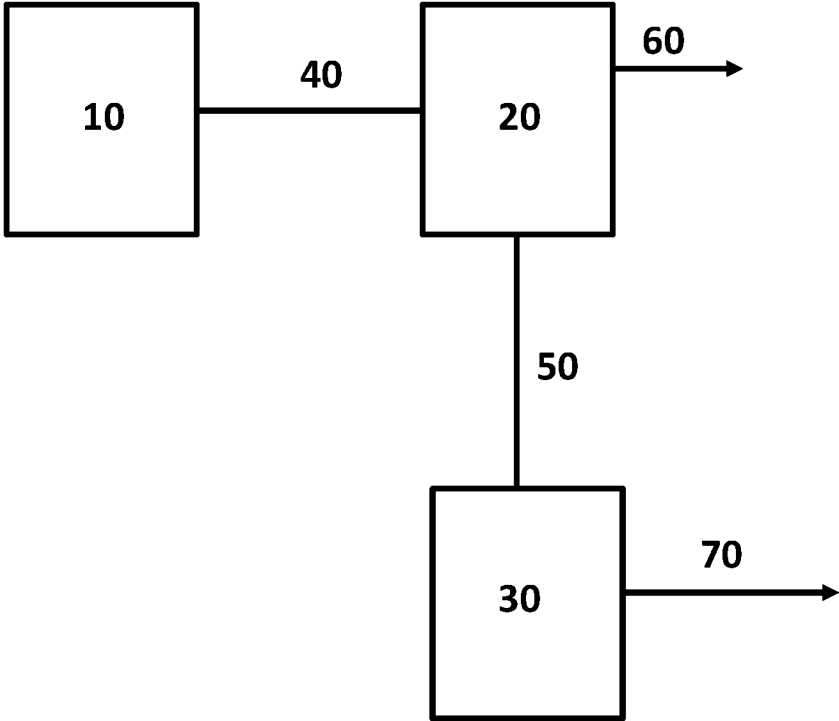
The calcination is carried out on a bed of catalyst. For example, if the calcination is carried out in a tray calciner, then the catalyst precursor added to the tray forms a bed which is typically kept stationary during the calcination. If the calcination is carried out in a rotary calciner, then the catalyst added to the rotary drum forms a bed that although not
5 stationary does maintain some form and shape as it passes through the calciner.

CLAIMS

1. A process for converting oxygenates into alkylate comprising:
 - a. feeding an oxygenate containing feed to an oxygenate to olefins conversion reactor;
 - b. contacting the oxygenate containing feed with a molecular sieve catalyst under oxygenate to olefins conversion conditions in the reactor to form a product stream comprising propylene, ethylene and mixed C4s;
 - c. separating the mixed C4s from the product stream to form a mixed C4 stream;
 - d. passing at least a portion of the mixed C4 stream to an alkylation process to produce alkylate.
2. The process of claim 1 further comprising removing isobutylene from the mixed C4 stream by contacting the mixed C4 stream with methanol or ethanol to form MTBE or ETBE before step d).
3. The process of any of claims 1-2 further comprising adding additional isobutane to step d).
4. The process of any of claims 1-3 wherein the alkylate comprises iso-octane.
5. The process of any of claims 1-4 wherein the alkylation process of step d) is a direct alkylation process.
6. The process of claim 5 wherein the direct alkylation process comprises reacting isobutane and mixed C4s in the presence of sulphuric or hydrofluoric acid.
7. The process of claim 1 wherein the alkylation process of step d) is an indirect alkylation process.
8. The process of claim 7 wherein the indirect alkylation process comprises dimerizing isobutylene in the mixed C4 stream over an acidic resin or a solid phosphoric acid to form alkylate.
9. The process of any of claims 7-8 further comprising producing a second mixed C4 stream in the indirect alkylation.

10. The process of claim 9 further comprising passing the second mixed C4 stream to a direct alkylation unit.
11. The process of claim 9 further comprising recycling the second mixed C4 stream to step a)
12. The process of claim 9 further comprising recycling the second mixed C4 stream to an olefin cracking reactor.

FIG. 1



INTERNATIONAL SEARCH REPORT

International application No.

PCT/US15/67569

A. CLASSIFICATION OF SUBJECT MATTER

IPC(8) - C07C 1/20, 1/22, 7/04 (2016.01)

CPC - C07C 1/20, 1/22, 7/04

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(8): C07C 1/00, 1/20, 1/22, 7/00, 7/04, 7/08 (2016.01)

CPC: C07C 1/00, 1/20, 1/22, 7/00, 7/04, 7/08, 2529/00, 2529/06, 2529/40

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 practicable, search terms used)

PatSeer (US, EP, WO, JP, DE, GB, CN, FR, KR, ES, AU, IN, CA, RU, AT, CH, TH, BR, PH, INPADOC Data), Google Patents, Google/Google Scholar, IEEE, EBSCO, feed, supply, provide, oxygenate, reactor, column, catalyst, molecular sieve catalyst, separate, distill, C4, alkylation, alkylate, iso-octane, iso-heptane

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X --- Y	US 2013/0172644 A1 (SHELL OIL COMPANY) 4 July 2013; abstract; figure 1; paragraphs [0006], [0008]-[0011], [0013]-[0014], [0017], [0034]-[0036], [0041]; claim 15	1-2 --- 3/1-2, 7-8, 9/7-8, 10/9/7-8, 11/9/7-8, 12/9/7-8
Y	EP 0,266,047 A2 (THE BRITISH PETROLEUM COMPANY P.L.C.) 4 May 1988; page 2, lines 26-27	3/1-2
Y	US 2010/0316536 A1 (VORA, BV et al.) 16 December 2010; figure 1; paragraphs [0014]-[0015], [0021]	7-8, 9/7-8, 10/9/7-8, 11/9/7-8, 12/9/7-8
Y	US 2009/0143629 A1 (VOSKOBOYNIKOV, TV) 4 June 2009; paragraphs [0006], [0011]	12/9/7-8

☐ 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 application or patent but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

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

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search

24 February 2016 (24.02.2016)

Date of mailing of the international search report

17 MAR 2016

Name and mailing address of the ISA/

Mail Stop PCT, Attn: ISA/US, Commissioner for Patents

P.O. Box 1450, Alexandria, Virginia 22313-1450

Facsimile No. 571-273-8300

Authorized officer

Shane Thomas

PCT Helpdesk: 571-272-4300

PCT OSP: 571-272-7774

INTERNATIONAL SEARCH REPORT

International application No.

PCT/US15/67569

Box No. II Observations where certain claims were found unsearchable (Continuation of item 2 of first sheet)

This international search report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:

2. ☐ Claims Nos.:
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:

3. ☒ Claims Nos.: 4-6
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box No. III Observations where unity of invention is lacking (Continuation of item 3 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

1. ☐ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.
2. ☐ As all searchable claims could be searched without effort justifying additional fees, this Authority did not invite payment of additional fees.
3. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:

4. ☐ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

Remark on Protest

- ☐ The additional search fees were accompanied by the applicant's protest and, where applicable, the payment of a protest fee.
- ☐ The additional search fees were accompanied by the applicant's protest but the applicable protest fee was not paid within the time limit specified in the invitation.
- ☐ No protest accompanied the payment of additional search fees.