

PROCESS FOR THE PRODUCTION
OF HIGH CETANE VALUE CLEAN FUELS

5 This invention relates to a process for the co-production of hydrocarbon lubricants and high cetane value hydrocarbon fuels from near linear alpha olefins derived from inexpensive lower alkenes by employing the intermediate production of near linear internal olefin oligomers.

10 The present invention provides a process for the co-production of lubricant range hydrocarbons and aromatics-free hydrocarbon fuel having high cetane number, comprising:

15 (a) contacting a feedstream comprising lower olefinic hydrocarbons with surface-deactivated, acidic, medium pore, shape selective metallocsilicate catalyst particles under oligomerization conditions whereby a product stream comprising aromatics-free, slightly branched internal olefin oligomers is produced;

20 (b) contacting the oligomers and ethylene with metathesis catalyst in a reaction zone under metathesis conditions whereby the internal olefin oligomers are converted to reaction product comprising slightly branched alpha-olefin oligomers and unconverted oligomers;

25 (c) contacting step (b) metathesis reaction product with reduced valence state Group VIB metal catalyst on porous support under oligomerization conditions and recovering a reaction product containing a 177°- 343°C (177°-343°C) fuel boiling range portion and a 343°C (650°F+) lubricant range portion;

30 (d) separating and hydrogenating step (c) fuel boiling range portion whereby a hydrocarbon fuel having cetane number between 50 and 75 and no



aromatics is produced.

5 The present invention further provides a process for the production of hydrocarbon fuels having high cetane value, comprising: contacting a feedstream comprising lower olefinic hydrocarbons with surface-deactivated acidic, medium pore, shape selective
10 metallosilicate catalyst particles under oligomerization conditions whereby a product stream comprising aromatics-free near linear olefinic oligomers is produced; hydrogenating at least a portion of the product stream and recovering a 177° - 343°C (350°-650°F) fuel boiling range fraction having a cetane value between 50 and 75, no aromatics and less than 0.5 weight % naphthenes.

15 In the processes known in the art for catalytic conversion of olefins to heavier hydrocarbons by catalytic oligomerization using a medium pore shape selective acid crystalline zeolite, such as ZSM-5 type catalyst, process conditions can be varied to favor the formation of hydrocarbons of varying molecular weight. At moderate temperature and relatively high
20 pressure, the conversion conditions favor C₁₀⁺ aliphatic product. Lower olefinic feedstocks containing C₂-C₈ alkenes may be converted. A typical reactive feedstock consists essentially of C₃-C₆ mono-olefins, with varying amounts of nonreactive paraffins and the like being acceptable components.

25 U.S. Patent Nos. 4,520,221, 4,568,786 and 4,658,079 to C. S. H. Chen et al, disclose further advances in zeolite catalyzed olefin oligomerization. These patents disclose processes for the oligomerization of light, or lower, olefins using zeolite
30 catalyst such as ZSM-5. The oligomers so produced are near linear in structure and contain internal olefin unsaturation. These unique olefinic oligomers are produced by surface deactivation of the ZSM-5 type



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catalyst by pretreatment with a surface-neutralizing base. The processes of Chen et al provide a particularly useful means to prepare slightly branched higher olefinic hydrocarbons from inexpensive lower olefins, particularly propylene.

5 In U.S. Patent No. 4,962,249, near linear higher olefinic hydrocarbons produced by the oligomerization of lower olefins using surface-deactivated zeolite catalyst are converted to a mixture comprising slightly branched and linear higher alpha olefins. These alpha olefins are oligomerized to lubricant
10 grade hydrocarbons in contact with cationic, Ziegler or coordination catalyst. Oligomerization of the aforementioned alpha olefins using reduced valence state Group VIB metal oxide catalyst on porous support provides a hydrocarbon lubricant with a viscosity
15 index of greater than 130 at 100°C. Olefin metathesis with ethene, as described in Olefin Metathesis by K. J. Ivin, published by Academic Press, Chapter 5, is applied to the internal olefinic oligomers of Chen et al to provide a route to the alpha olefins suitable
20 for the production of synthetic lubricants, utilizing the process described in U.S. Patent Nos. 4,827,064 and 4,827,073 to M. Wu. The lubricants recovered comprise the 650°F+ (343°C+) fraction of the oligomerization reaction product.

25 It has been found that the 177° - 343°C (350° - 650°F) portion of the product from the oligomerization of light olefin with surface-deactivated shape selective medium pore zeolite catalyst particles comprises olefinic hydrocarbons having unique and
30 desirable structures as precursors for high cetane value clean fuels where, in this invention, the term clean fuels relates particularly to the absence of aromatics in the fuel. These oligomers are near



linear in structure and contain no aromatics. As a result, following hydrogenation they produce cetane values between 50 and 75. When the near linear olefinic hydrocarbons from surface-deactivated zeolite-catalyzed oligomerization of light olefins are subjected to ethene metathesis to alpha olefins and oligomerization following the process of in U.S. Patent No. 4,962,249, the overall process reaction product comprises a mixture of a 343°C+ (650°F+) portion comprising high VI lubricant and a 177° - 343°C (350°-650°F) portion comprising high cetane clean fuels precursor. Hydrogenation of the 177°- 343°C (350°-650°F) portion provides an aromatics-free fuel with a cetane value between 50-75. Accordingly, the combined process results in the co-production of high cetane clean fuels and high VI synthetic lubricant.

Figure 1 is a graph of the GC results of the (A) propylene oligomers of Example IV.

Figure 2 is a graph of the GC results of the (B) propylene oligomers of Example IV.

The olefin oligomers used as starting material in the present invention are prepared from C₃-C₅ olefins according to the methods presented by Chen et al in the aforementioned patents cited and N. Page and L. Young in U.S. Patent No. 4,855,527. Shape-selective oligomerization, as it applies to conversion of C₃-C₅ olefins over ZSM-5, is known to produce higher olefins up to C₃₀ and higher. Reaction conditions favoring higher molecular weight products are low temperature (200°-260°C), elevated pressure (about 2000 kPa or greater) and long contact times (less than 1 WHSV). The reaction under these conditions proceeds through the acid catalyzed steps of oligomerization, isomerization-cracking to a mixture of intermediate carbon number olefins, and interpolymerization to give

a continuous boiling product containing all carbon numbers. The channel system of ZSM-5 type catalysts impose shape selective constraints on the configuration of large molecules, accounting for the differences with other catalysts.

5 The shape-selective
oligomerization/polymerization catalysts preferred for
use herein to prepare the olefin oligomers used as
starting material in the invention include the
crystalline aluminosilicate zeolites having a silica
to alumina molar ratio of at least 12, a constraint
10 index of about 1 to 12 and acid cracking activity of
about 50-300. Representative of the ZSM-5 type
zeolites are ZSM-5, ZSM-11, ZSM-12, ZSM-23, ZSM-35 and
ZSM-38. ZSM-5 is disclosed and claimed in U.S. Patent
No. 3,702,886 and U.S. Patent No. Re. 29,948; ZSM-11
15 is disclosed and claimed in U.S. Patent No. 3,709,979.
Also, see U.S. Patent Nos. 3,832,449 for ZSM-12;
4,076,842 for ZSM-23; 4,016,245 for ZSM-35 and
4,046,839 for ZSM-38. A suitable shape selective
medium pore catalyst for fixed bed is a small crystal
20 H-ZSM-5 zeolite (silica:alumina ratio =70:1) with
alumina binder in the form of cylindrical extrudates
of about 1-5mm. Unless otherwise stated in this
description, the catalyst shall consist essentially of
ZSM-5, which has a crystallite size of about 0.02 to
25 0.05 micron, or ZSM-23. Other pentasil catalysts
which may be used in one or more reactor stages
include a variety of medium pore siliceous material
disclosed in U.S. Patent Nos. 4,414,423 and 4,417,088.

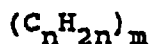
30 The acid catalysts are deactivated by pre-
treatment with a surface-neutralizing base, as
disclosed by Chen et al and Page et al in the
aforementioned patents. Surface deactivation is
carried out using bulky or sterically hindered bases,
typically those comprising trialkyl substituted

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pyridines. These hindered bases have very limited access to the internal pore structure of the catalyst, leaving the pores active sites for near linear oligomerization. However, active surface sites which are not constrained, as pores are, to low branching oligomerization are neutralized.

5 Considering propylene oligomerization for purposes of illustration, the olefinic oligomerization-polymerization products include C_{10}^{+} substantially linear aliphatic hydrocarbons. The ZSM-5 catalytic path for propylene feed provides a long
10 chain with approximately one to two lower alkyl (e.g., methyl) substituents per 12 carbon atoms in the straight chain.

 When propylene or butene are oligomerized according to processes described herein, a unique
15 mixture of liquid hydrocarbon products are formed. More particularly, this mixture of hydrocarbons may comprise at least 95% by weight of mono-olefin oligomers of the empirical formula:



20 where n is 3 or 4 and m is an integer from 1 to approximately 10, the mono-olefin oligomers comprising at least 20% by weight of olefins having at least 12 carbon atoms. Those olefins having at least 12 carbon atoms have an average of from 0.80 to 2.50 methyl side groups per carbon chain. The olefin side groups are
25 predominantly methyl.

 It will be understood that methyl side groups are methyl groups which occupy positions other than the terminal positions of the first and last (i.e., alpha and omega) carbon atoms of the longest carbon chain.
30 This longest carbon chain is also referred to herein as the carbon backbone chain of the olefin. The average number of methyl side groups for the C_{12}

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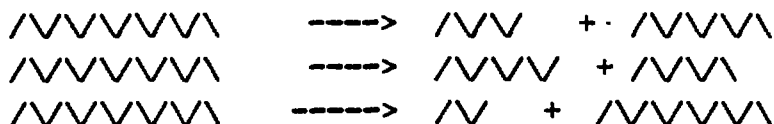
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2) from disubstituted olefins



The equilibrium is displaced to the right in the presence of excess ethylene.

5 The reaction produces linear alpha olefins, branched alpha olefins and vinylidene olefins. The structure and molecular weight of the product olefins depend on the structure of the starting oligomers. For olefins of carbon number C_n which have undergone the metathesis with ethylene, the product olefins have an average molecular weight, on a molar basis, of $C_{n/2}+1$. Trisubstituted olefins account for a major share of olefins in the slightly branched olefin oligomers. Where these trisubstituted olefins are isoolefinic they account for a major share, as well, of the methyl branching in the olefin oligomer. Their reaction in metathesis with ethylene produces an alpha olefin and a vinylidenic olefin, as already shown. Further, it is known that vinylidene olefins are unreactive in reduced chromium oxide catalyzed and Ziegler catalyst catalyzed oligomerization. Accordingly, the olefin metathesis reaction of slightly branched olefin described here produces a mixture of olefins where only a portion, alpha olefins, are oligomerizable with Ziegler or chromium catalyst to higher lubricant grade hydrocarbon oligomers. A large portion of the methyl branching in the starting olefins is effectively removed from inclusion in higher oligomers produced by coordination catalyst by conversion to vinylidene structures through metathesis with ethylene.

25 In general any of the C_{2-8} alpha olefins can be reacted with the oligomerization product effluent in the metathesis operation herein. Some specific

examples of such alpha olefins are ethylene, propylene, 1-butene, 1-pentene, 1-hexene, 1-octene, and the like with ethylene being preferred.

Any of the catalysts heretofore employed in olefin metathesis are suitably utilized in the metathesis conversion herein. Many of these catalyst have been reported in the prior art. Preferably, the catalyst is one of molybdenum, tungsten, or rhenium oxide deposited on a support of silica, alumina, silica-alumina or aluminum phosphate. An additional metal oxide, e.g., a rare earth metal oxide, can also be present as is known. Prior to its use, the catalyst is activated by calcination carried out in a conventional manner. A particularly suitable catalyst is molybdenum oxide supported on a mixture of amorphous precipitated silica and colloidal silica. A preferred catalyst is rhenium oxide on alumina. Co-catalysts, including tetraalkyl tin, are useful. A particularly preferred catalyst is rhenium oxide on gamma-alumina plus tetramethyl tin co-catalyst.

Suitable conditions for the metathesis reaction include a pressure of from 50-35000 KPa, a temperature of from 0°C to about 500°C, and space velocities of from 1 to about 300 WHSV based on the nature of the metathesis catalyst. Although the activity of the catalyst is suitable within the broad ranges mentioned above, increased activity is generally found when the pressure is from 700 to about 3500 KPa, the temperature range is from 20°-100°C, and the WHSV is from 0.5 to about 1000. The process can be carried out either in the presence or absence of a diluent. Diluents comprising paraffinic and cycloparaffinic hydrocarbons can be employed. Suitable diluents are, for example, propane, cyclohexanes, methylcyclohexane, normal pentane, normal hexane, isooctane, dodecane, and the like, or mixtures thereof, including primarily

those-paraffins and cycloparaffins having up to 12 carbon atoms per molecule. The diluent should be nonreactive under the conditions of the reaction. The reaction can also be carried out in a single unit or a battery of units employing the same or a different catalyst.

5 The amount of alpha-olefin employed in the metathesis conversion can vary widely and will depend in part on the degree of unsaturation in the higher olefin feed which can be readily quantified employing known techniques, e.g., bromine number. Generally,
10 the alpha-olefin, particularly, will be present in stoichiometric excess of the amount theoretically required but can be substantially less than this. The amount of alpha olefin should be an amount sufficient to suppress the self-metathesis reaction which can
15 occur between two molecules of the near linear olefin feedstock. When ethylene is used as the alpha olefin that amount is typically about a two to five molar excess. If desired, excess alpha-olefin can be separated from the metathesis product effluent and
20 recycled to this stage.

 It has been discovered that in the metathesis reaction between the near linear higher olefins and ethylene trisubstituted olefins, the ethylene
 trisubstituted olefins are less active than
25 disubstituted olefins. The conversion of disubstituted olefins proceeds effectively at ambient temperature (23°C) in the presence of a co-catalyst $\text{Sn}(\text{CH}_3)_4$, or at 75°-100°C in the absence of a co-catalyst $\text{Sn}(\text{CH}_3)_4$. Trisubstituted olefins, i.e.,
30 those containing isoolefin groups, are not converted in the absence of a co-catalyst $\text{Sn}(\text{CH}_3)_4$ even at elevated temperature (75°C). Optionally, this relationship can be readily utilized to reduce the extent of trisubstituted olefin metathesis to produce

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vinylidene olefins in favor of predominantly disubstituted olefin metathesis with ethylene to produce alpha olefins.

5 The primary purpose of performing co-metathesis reactions of near-linear propylene oligomers with ethylene is to produce alpha olefins. The alpha olefins so produced are complex mixtures containing two types of structures. One type is linear, but contains both even and odd number carbons, and a mixture of different molecular weights. The other is
10 near-linear with one or two methyl branches, and also contain both even and odd number carbons, and a mixture of different molecular weights. Alpha-olefins are known to be polymerizable by chromium catalysis to produce high VI lubricants.

Alpha Olefin Oligomerization

15 The olefins used to prepare lubes and high cetane value fuels products herein are from the co-metathesis reactions between propylene oligomers and ethylene. The lubes and fuel products were prepared by using activated Cr (3%) on silica catalyst as described in
20 the previously cited U.S. Patents to M. Wu. The low branch ratio lubes comprise the 343°C+ (650°C+) fraction of the oligomerization product recovered preferably by distillation.

25 The near linear alpha olefins oligomerized in this invention to provide high VI lubricant are characterized as having branching confined predominantly to the pendant alkyl group of the oligomer lubricant molecule. While it is known and taught in the cited Wu patents that branching in the
30 backbone of the lubricant molecule adversely effects VI, high VI lubes can be prepared from slightly branched alpha olefins by reduced chromium catalysis if those branches are restricted predominantly to the pendant alkyl group of the oligomer molecule.

High Cetane Value Fuel Recovery

The 343°C+ (650°F+) lubes described above are co-produced with 343°C- (650°F-) products in 3 steps:

(1) shape selective oligomerization of lower olefins (e.g., propylene) to higher, near-linear internal olefins;

5 (2) co-metathesis reaction of the near-linear olefins with ethylene to 1-olefins; and

(3) polymerization of the resulting alpha olefins by chromium catalysis to high VI lubes and 650°F- products.

10 The 177°-343°C (350°-650°F) portion of the 343°C- (650°F-) products have unique and desirable structures as precursors for high cetane clean fuels. They contain both the initial near-linear oligomers unconverted in step 2 and vinylidene olefins formed in
15 step 2 but not polymerized by Cr catalysis in step 3. After hydrogenation, these products exhibit high cetane numbers as determined by a reliable H NMR method and low temperature ignition behavior. Cetane number was also determined on several samples by ASTM
20 method.

The 177°-343°C (350°-650°F) fraction of the near-linear internal olefins obtained in step 1 is also a precursor of high cetane clean fuels. The present
25 fuel precursors contain a significant portion of vinylidene olefins as well as near-linear internal olefins. After hydrogenation, the fuels contain paraffins with 1 to 2 methyl side chains per main chain, derived from the near-linear internal olefins. A significant portion will have only one methyl side
30 chain on number 2 carbon atom of the main chain, as derived from the vinylidene olefins. There are no aromatics present in either fuel derived from near linear internal olefins from zeolite catalyzed oligomerization of lower olefins or from reduced
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chromium catalyzed oligomerization of alpha olefins, as produced from the foregoing steps 1-3. After hydrogenation, the fuels have cetane numbers ranging from 55 to 75, as determined by ASTM method and/or from NMR analysis.

The following Examples illustrate the process of the present invention for the production of high cetane value clean fuels.

Example I

Near-linear internal olefins are prepared by oligomerization of propylene in a continuous stirred tank reactor (CSTR) using surface-deactivated ZSM-23 as the catalyst at 200°C, 900 psig and 0.3 weight hourly space velocity (WHSV) in a single pass. The conversion of propylene is 91%. The product oligomers contain 21.4% of internal olefins having a carbon number equal to or less than C_{11} and 78.6% of internal olefins having a carbon number equal to or greater than C_{12} .

The C_{11} - olefins are removed by fractional distillation. For the co-metathesis reaction with ethylene, the C_{12}^{+} olefins are purified by percolating through activated alumina followed by treating with Zeolite 13X and Catalyst R3-11 (Chemical Dynamics Corporation). Activated Re_2O_7/Al_2O_3 containing 12% Re and Sn $(CH_3)_4$ at 1:1 mole ratio are used as co-catalysts. The co-metathesis reaction is carried out in a 750 ml Parr reactor equipped with two gas inlets and a sampling dip tube with filter at its tip. A catalyst addition device with a door at its bottom, which could be opened by applying a pressure, is attached to a gas inlet under the reactor cap above the reaction mixture. In a glove box, 75 grams of the purified oligomers is charged into the Parr reactor. The catalyst device is detached from the reactor cap and 6 grams of the activated $Re_2O_7/-Al_2O_3$ are weighed



into the device. The $\text{Sn}(\text{CH}_3)_4$ is syringed into the catalyst device from its solution in the oligomers making certain that the catalyst is evenly wet. The catalyst device is reattached and the Parr reactor is closed. The reactor is then taken out of the glove box and assembled in the laboratory. Two hundred psi ethylene is introduced into the reactor through one gas inlet, and while stirring, the rest of the ethylene (a total of 800 psi) is introduced through the other gas inlet to which the catalyst device is attached. The pressure pushes the door open and the catalyst is carried into the reaction mixture by the incoming ethylene. The reaction mixture is kept at the ambient temperature (25°C). Liquid samples are withdrawn periodically and analyzed by GC. The reaction takes about 24 hours to reach equilibrium at which time 80% of the oligomers are co-metathesized. The excess ethylene is discharged and the reactor while still closed is carried back to the glove box where the product is discharged and used directly for reduced Cr/SiO_2 catalyzed polymerization according to the previously cited process of M. Wu. Fifty grams of the liquid product and 4 grams of activated Cr/SiO_2 (3% Cr) are charged into a 450 ml Parr reactor. The reactor is closed, taken out of the glove box and assembled in the laboratory for polymerization. The temperature is raised to 110°C and kept there for 24 hours. The reactor is cooled down and opened. The catalyst is filtered off by suction and the water-white product is hydrogenated over Pd/C at 50°C and distilled in vacuum to obtain the following products:

650+°F lube:

Yield: 54.1%, Viscosity at 100°C: 50cS; VI: 164;
480°-650°F diesel fuel:

Yield: 20.5%, NMR estimated cetane number 68; no aromatics

Ignition behavior: T5 = 245.9°C; T10 = 236.8°C;

T20 = 229.8°C;

350°-480°F kerosene/jet fuel:

Yield: 15.0%.

<350°F: Yield: 10.4%.

Example II.

5 In this example the same starting propylene
oligomers are used in the co-metathesis reaction with
ethylene and under the same experimental conditions as
in Example I. The co-metathesis conversion is 75%
based on the propylene oligomers. In the Cr/SiO₂
10 catalyzed polymerization step, 72.5 grams of olefins
and 4 grams of Cr/SiO₂ (3% Cr) are used. The
polymerization is carried out at 110°C for 116 hours.
After hydrogenation over Pd/C at 50°C and distillation
in vacuum the following products are obtained:

15 343°C+ (650°F+) lube:

Yield: 47.6%;

Viscosity at 100°C: 35 cS;

VI: 159;

249°-343°C (480°-650°F) diesel fuel:

20 Yield: 24.5%

NMR estimated cetane number: 71; no aromatics

Ignition behavior: T5 = 244.7°C; T10 = 235.7°C;

T20 = 229.7°C;

177°-249°C (350°-480°F) kerosene/jet fuel:

25 Yield: 15.9%;

<177°C (<350°F):

Yield: 12.0%;

Example III

30 Near-linear internal olefins are prepared by
oligomerization of propylene in a continuous stirred
tank reactor (CSTR) with <C12 olefins recycled to
extinction at 210°C and 0.3 WHSV. The conversion of
propylene is 90%. The product oligomers which are
near-linear internal olefins are subjected to co-

metathesis with ethylene (80% conversion) followed by polymerization catalyzed by Cr/SiO_2 in the same manner as described in Example I. After hydrogenation and distillation, the following products are obtained:

343°C+ (650°F+) lube:

Yield: 55.2%,

Viscosity at 100°C: 44.7 cS,

VI: 153;

249°-343°C (480°-650°F) diesel fuel:

Yield: 25.4%;

177°-249°C (350°-480°F) kerosene/jet fuel:

Yield: 13.8%

NMR estimated cetane number: 56; no aromatics

Ignition behavior: T5 = 251.4°C, T10 =

237.4°C;

T20=231.0°C;

<177°C (<350°F):

Yield: 5.6%

A further embodiment of the instant invention comprises the discovery that the <343°C- (<650°F-) fraction of near-linear paraffins recovered from the oligomerization of lower olefins using surface-deactivated zeolite as catalyst, as taught in the cited references of Chen and Page, contain after hydrogenation diesel and kerosene boiling range aromatics-free fuels that exhibit high cetane values. Near-linear oligomers after hydrogenation yield slightly methyl branched paraffins which yield superior autoignition and low temperature performance properties desired in diesel fuels. In addition the high H/C ratio in these fuels lead to reduced particulate emissions when burned in diesel engines.

These embodiments of the present invention are illustrated in the following Example.

Example IV

For comparison, two different batches of propylene oligomers are used. Both are prepared by using as the catalyst ZSM-23 surface-deactivated by 2,4,6-collidine.

One batch (A) is prepared in a semi-continuous stirred tank reactor without recycle. The oligomerization is carried out at 200°C, 1000 psig with propylene fed on demand. The composition is shown in Table I and Figure 1. The other batch (B) is prepared in twin fixed-bed reactors and with recycle of the C_{12} olefin oligomers (3:1 liquid) to extinction. The conditions are 230°C, 1000 psig, and WHSV of 0.2. The compositions are shown in Table II and Figure 2.

The oligomers are fractionated under a reduced pressure using a ASTM D-2892 still to boiling point ranges close to number 1 fuel (B.P.: 177°-249°C (350°-480°F) and diesel fuel (B.P.: 249°-343°C (480°-650°F)). The fractions are hydrogenated at 150°C using Ni on Kieselgel until no more hydrogen is taken up. The lack of olefin content of the final products is established by NMR. Cetane number, API gravity, freezing point are determined by the respective ASTM methods.

TABLE I
PROPYLENE OLIGOMERS PREPARED
SINGLE PASS IN A CSTR

(A)

EXPERIMENTAL CONDITIONS

Catalyst: ZSM-23 treated with 2,4,6-collidine
Feed: Propylene, fed on demand
Temperature: 200°C
Pressure: 1000 psig

COMPOSITION

<u>Component</u>	<u>Wt. %</u>
C ₆	43.0
C ₉	25.2
C ₁₂	14.8
C ₁₅	9.6
C ₁₈	3.9
C ₂₁ and higher	3.4

BRANCHING

<u>Component</u>	<u>Isomer</u>	<u>Wt. %</u>
C ₉	Di-Me	18.8
	Mono-Me	72.4
	Normal	8.9
	Me/C ₉	1.19
C ₁₂	Di-Me	22.9
	Mono-Me	69.4
	Normal	7.7
	Me/C ₁₂	1.27
C ₁₅	Di-Me	18.7
	Mono-Me	74.1
	Normal	7.3
	Me/C ₁₅	1.21

TABLE II
Propylene Oligomers Prepared
in Twin Fixed-Bed Reactors
With C_{12} = Recycled To Extinction
(B)

EXPERIMENTAL CONDITIONS

Catalyst: ZSM-23 treated with 2,4,6-collidine
 Feed: Propylene (60%) + Propane (40%)
 WHSV: 0.2 based on propylene
 Temperature: 230°C
 Pressure: 1000 psig
 Recycle: 3:1 liquid, to extinction

COMPOSITION

<u>Component</u>	<u>Wt. %</u>
C ₆	2.7
C ₉	4.9
C ₁₂	47.5
C ₁₅	26.4
C ₁₈	11.0
C ₂₁ and higher	7.2

BRANCHING

<u>Component</u>	<u>Isomer</u>	<u>Wt. %</u>
C ₁₂	Di-Me	55.2
	Mono-Me	41.2
	Normal	3.6
C ₁₅	Me/C ₁₂	1.79
	Di-Me	--
	Mono-Me	--
	Normal	--
	Ne/C ₁₅	1.75

The yield and diesel properties from the two propylene oligomers after hydrogenation are summarized in Table III. It should be noted that propylene oligomers (olefins) are the only products from the

oligomerization process and, as a result, the hydrogenated products have paraffinic structures only. Results of the GC/MS showed that greater than 96 wt% of the 177°-249°C (350°-480°F) fraction is positively identified as C_nH_{2n+2} paraffins by their molecular ions and fragmentation patterns; 3.0 wt% have no molecular ions; however, they show fragmentation which could be derived from C_nH_{2n+2} paraffins. Only 0.4 wt%, by total ion integration, could belong to C_nH_{2n} (olefins which were not completely hydrogenated or cycloalkanes, otherwise known as naphthenes). The 249°-343°C (480°-650°F) fraction gave GC/MS results which showed all peaks are positively identified as C_nH_{2n+2} paraffins by their molecular ions.

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TABLE III
FUEL YIELD AND PROPERTIES
FROM HYDROGENATED PROPYLENE OLIGOMERS

(A) Oligomers - CSTR single pass, $1.3\text{CH}_3/12\text{C}$:

Boiling Range, °C (°F)	Yield %	Cetane Number	API Gravity	F.P. °C	Mid BP °F
177-316 (350-600)	31.7	60.6	52.7	-54.4	-
177-249 (350-480)	14.5	59.4	54.1	-62.5	424
249-343 (480-650)	17.2	73.7	48.4	-19.3	539

(B) Oligomers - 2 fixed bed reactors, C_{12} = recycle,
 $1.8\text{CH}_3/12\text{C}$

177-343 (350-650)	90.0	63.2	50.7	-1.0	499
177-249 (350-480)	44.0	57.7	55.1	-73.0	435
249-343 (480-650)	46.0	65.3	48.4	-22.6	574

The foregoing Example illustrates the surprising discovery that particularly high cetane value fuels free of aromatics are recoverable following hydrogenation of the 343°C- (650°F-) fraction of the oligomerization product of propene using surface-deactivated catalyst. These oligomers have a unique near linear structure as shown by NMR. This unique structure, it is believed, is the distinguishing element responsible for providing such surprisingly high cetane values in a clean fuel free of aromatics.

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CLAIMS:

1. A process for the co-production of lubricant range hydrocarbons and aromatics-free hydrocarbon fuel having high cetane number, comprising:

5 (a) contacting a feedstream comprising lower olefinic hydrocarbons with surface-deactivated, acidic, medium pore, shape selective metallocsilicate catalyst particles under oligomerization conditions whereby a product stream comprising aromatics-free, slightly branched internal olefin oligomers is produced;

(b) contacting the oligomers and ethylene with metathesis catalyst in a reaction zone under metathesis conditions whereby the internal olefin oligomers are converted to reaction product comprising slightly branched alpha-olefin oligomers and unconverted oligomers;

15 (c) contacting step (b) metathesis reaction product with reduced valence state Group VIB metal catalyst on porous support under oligomerization conditions and recovering a reaction product containing a 177°- 343°C (350°-650°F) fuel boiling range portion and a 343°C (650°F+) lubricant range portion;

20 (d) separating and hydrogenating step (c) fuel boiling range portion whereby a hydrocarbon fuel having cetane number between 50 and 75 and no aromatics is produced.

2. The process of claim 1 wherein the lower olefinic hydrocarbons comprise C₂-C₄ 1-alkenes.

3. The process of claim 2 wherein the hydrocarbons comprise propene.

4. The process of claim 1 wherein the slightly branched internal olefin oligomer portion comprise hydrocarbons having about 1-2 methyl branches per 12 carbon atoms.



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5. The process of claim 1 wherein the metathesis catalyst includes supported oxides of rhenium, molybdenum or tungsten.

6. The process of claim 5 further including tetraalkyl tin as co-catalyst.

7. The process of claim 5 wherein the catalyst comprises aluminum oxide supported rhenium oxide and tetramethyl tin.

8. The process of claim 1 wherein the metallosilicate catalyst includes surface-deactivated ZSM-5 or ZSM-23.

9. The process of claim 1 wherein step (c) catalyst comprises CO-reduced chromium oxide catalyst on silica support.

10. The process of claim 1 including the further steps of separating step (a) product stream to recover a $C_{11}+$ oligomer portion and reacting the $C_{11}+$ oligomer in step (b).

11. A process for the production of hydrocarbon fuels having high cetane value, comprising: contacting a feedstream comprising lower olefinic hydrocarbons with surface-deactivated acidic, medium pore, shape selective metallosilicate catalyst particles under oligomerization conditions whereby a product stream comprising aromatics-free near linear olefinic oligomers is produced;

hydrogenating at least a portion of the product stream and recovering a $177^{\circ} - 343^{\circ}\text{C}$ ($350^{\circ} - 650^{\circ}\text{F}$) fuel boiling range fraction having a cetane value between 50 and 75, no aromatics and less than 0.5 weight % naphthenes.

12. The process of claim 11 wherein the lower olefinic hydrocarbons comprise C_2-C_4 1-alkenes.

13. The process of claim 12 wherein the hydrocarbons comprise propene.

14. The process of claim 11 wherein the



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metallo-silicate catalyst is surface-deactivated ZSM-5 or ZSM-23.

15. The process of claim 11 wherein the near linear olefinic oligomers comprise hydrocarbons having about 1-2 methyl branches per 12 carbon atoms.

16. A hydrocarbon fuel composition having high cetane value comprising the reaction product of a process comprising the steps of:

5 (a) contacting a feedstream comprising lower olefinic hydrocarbons with surface-deactivated, acidic, medium pore, shape selective metallo-silicate catalyst particles under oligomerization conditions whereby a product stream comprising aromatics-free, slightly branched internal olefin oligomers is
10 produced;

(b) contacting the oligomers and ethylene with metathesis catalyst in a reaction zone under metathesis conditions whereby the internal olefin oligomers are converted to reaction product comprising
15 slightly branched alpha-olefin oligomers and unconverted oligomer;

(c) contacting step (b) metathesis reaction product with reduced valence state Group VIB metal catalyst on porous support under oligomerization
20 conditions and recovering a reaction product containing a 177°-343°C (350°-650°F) fuel boiling range portion and a 343°C+ (650°F+) lubricant range portion;

(d) separating and hydrogenating step (c) fuel
25 boiling range portion containing no aromatics and less than 0.5 wt % naphthenes whereby a clean hydrocarbon fuel having cetane number between 50 and 75 is produced.

17. The process of claim 16 wherein the lower olefinic hydrocarbons comprise propene.

18. The process of claim 16 wherein the slightly branched internal olefin oligomer portion comprise hydrocarbons having about 1-2 methyl branches per 12



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carbon atoms.

19. The process of claim 16 including the further steps of separating step (a) product stream to recover a $C_{11}+$ oligomer portion and reacting the $C_{11}+$ oligomer in step (b).

5 20. A hydrocarbon fuel composition having high cetane number, comprising: an aromatics-free mixture of near-linear paraffinic hydrocarbons having a boiling range between 177° - 343° C (350° - 650° F), cetane number between 50 and 75 and containing less than 0.5 wt % naphthenes, the hydrocarbons containing about 1-2 methyl branches per 12 carbon atoms.

