

MULTIPLE FEED PROCESS FOR THE PRODUCTION OF PROPYLENE

Statement of Related Applications

USSN 09/072,632 and USSN 09/073,085 are related to this application.

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Field of the Invention:

This invention relates to a process to produce propylene from a hydrocarbon feed stream containing C₅'s and/or C₆'s, preferably a naphtha feed stream, where multiple feeds are used to feed portions of the feed stream into different portions of the reactor, or into different reactors.

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Background of the Invention:

Propylene is an important chemical of commerce. In general propylene is largely derived from selected petroleum feed materials by procedures such as steam cracking which also produces high quantities of other materials. At times, there exists shortages of propylene which result in uncertainties in feed supplies, rapidly escalating raw material costs and similar situations which are undesirable from a commercial standpoint. Also due to imbalances in hydrocarbon values, economics often favor using feedstocks or operating conditions in steam cracking which produce less propylene provided an effective process for forming propylene was available. Methods are known for the conversion of higher hydrocarbons to reaction mixtures comprised of the C₂ and C₃ lighter olefins. For example, EP 0 109 059 A and EP 0 109 060 A provide illustrative disclosures of conditions and catalysts which are effective for the conversion of higher hydrocarbons such as butenes to the lighter olefins. USSN 07/343,097 likewise is believed to provide a detailed disclosure of prior methods for the production of lower olefins from higher hydrocarbon feed materials. In certain instances, it would be very advantageous to provide means for still further improving yields of propylene which result from the conversion of less expensive higher hydrocarbon feed materials.

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Prior methods to produce propylene include:

1. The disproportionation or metathesis of olefins. See for example US patents 3,261,879; 3,883,606; 3,915,897; 3,952,070; 4,180,524; 4,431,855; 4,499,328; 4,504,694; 4,517,401; 4,547,617.
- 5 2. US 5,026,936 which discloses the selective production of propylene for C4 and higher hydrocarbons by reacting the feed with a zeolite, then the ethylene produced is passed to a metathesis zones where it is further converted to propylene. See also, U.S. Pat. Nos. 5,026,935; 5,171,921 and 5,043,522.
3. US 5,043,522 which discloses using ZSM-5 with C4+ feeds to produce
10 lighter olefins including propylene.
4. U.S. Patent No. 4,830,728 discloses a fluid catalytic cracking (FCC) unit that is operated to maximize olefin production. The FCC unit has two separate risers into which a different feed stream is introduced. The operation of the risers is designed so that a suitable catalyst will act to convert a heavy gas oil in one
15 riser and another suitable catalyst will act to crack a lighter olefin/naphtha feed in the other riser. Conditions within the heavy gas oil riser can be modified to maximize either gasoline or olefin production. The primary means of maximizing production of the desired product is by using a specified catalyst.
5. U.S. Patent No. 5,069,776 teaches a process for the conversion of a
20 hydrocarbonaceous feedstock by contacting the feedstock with a moving bed of a zeolitic catalyst comprising a zeolite with a pore diameter of 0.3 to 0.7 nm, at a temperature above about 500°C and at a residence time less than about 10 seconds. Olefins are produced with relatively little saturated gaseous hydrocarbons being formed. Also, U.S. Patent No. 3,928,172 teaches a process for
25 converting hydrocarbonaceous feedstocks wherein olefins are produced by reacting said feedstock in the presence of a ZSM-5 catalyst.

6. Concurrently pending USSN 09/072,632 discloses a method to improve the yield of propylene by selecting certain reaction conditions and certain catalysts.

Thermal and catalytic conversion of hydrocarbons to olefins is an important industrial process producing millions of pounds of olefins each year. Because of the large volume of production, small improvements in operating efficiency translate into significant profits. Catalysts play an important role in more selective conversion of hydrocarbons to olefins.

While important catalysts are found among the natural and synthetic zeolites, it has also been recognized that non-zeolitic molecular sieves such as silicoaluminophosphates (SAPO) including those described in U. S. Patent 4,440,871 also provide excellent catalysts for cracking to selectively produce light hydrocarbons and olefins. The SAPO molecular sieve has a network of AlO_4 , SiO_4 , and PO_4 tetrahedra linked by oxygen atoms. The negative charge in the network is balanced by the inclusion of exchangeable protons or cations such as alkali or alkaline earth metal ions. The interstitial spaces or channels formed by the crystalline network enables SAPOs to be used as molecular sieves in separation processes and in catalysis. There are a large number of known SAPO structures. The synthesis and catalytic activity of the SAPO catalysts are disclosed in U. S. Patent 4,440,871.

SAPO catalysts mixed with zeolites (including rare earth exchanged zeolites) are known to be useful in cracking of gasoils (U. S. Patent 5,318,696). U. S. Patents 5,456,821 and 5,366,948 describe cracking catalysts with enhanced propylene selectivity which are mixtures of phosphorus treated zeolites with a second catalyst which may be a SAPO or a rare earth exchanged zeolite. Rare earth treated zeolite catalysts useful in catalytic cracking are disclosed in U. S. Patents 5,380,690, 5,358,918, 5,326,465, 5,232,675 and 4,980,053. Thus there is a need in the art to provide more processes to increase the yields of propylene produced from higher olefin feed stocks such as naphtha feed stocks.

Summary of the Invention:

This invention relates to a process to produce propylene from a hydrocarbon feed stream comprising C₅ and/or C₆ components comprising introducing the light portion of the hydrocarbon feed stream into a reactor containing one or more catalysts separately from the heavy portion of the hydrocarbon feed stream, wherein the light portion of the feedstream comprises that portion that boils at 120°C or less, and the heavy portion of the feed stream is that portion left over after the light portion is removed.

Brief Description of the Drawings:

Figures 1 and 2 depict possible configurations for the multiple feeds into one or more reactors. In Figure 2, A and B are different catalysts.

Detailed Description of the Invention:**Hydrocarbon Feed Stream**

This invention particularly relates to a process to produce propylene from a hydrocarbon feed stream containing C₅ and /or C₆ components comprising introducing the light portion of the hydrocarbon feed stream into a reactor separately from the heavy portion of the hydrocarbon feed stream, where the light portion is that portion that has a boiling point range of 120 °C or less, more preferably 100 °C or less, even more preferably 80 °C or less. The heavy portion of the hydrocarbon feed stream is the portion left over after the light portion has been removed. In a preferred embodiment the light portion comprises C₅ and/or C₆ components. In a particularly preferred embodiment the light portion comprises at least 50 weight%, preferably at least 75 weight%, more preferably at least 90 weight%, more preferably at least 98 weight%, of the C₅ and/ or C₆ components present in the hydrocarbon feed stream, preferably a light catalytically cracked naphtha feed stream. In another embodiment, the light portion comprises at least 50 weight%, preferably at least 75 weight%, more preferably at least 90 weight%, more preferably at least 98 weight%, of the C₅ component present in the hydrocarbon feed stream, preferably a light catalytically cracked naphtha feed stream.

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By C₅ and C₆ components is meant a hydrocarbon feed stream containing linear, branched or cyclic paraffins, olefins, or aromatics, having 5 or 6 carbon atoms, respectively. Examples include pentane, cyclopentene, cyclopentane, cyclohexane, pentene, pentadiene cyclopentadiene, hexene, hexadiene, and benzene.

The heavy portion of the hydrocarbon feed stream typically includes hydrocarbons having one more carbon than those in the light portion. In one embodiment the heavy component comprises hydrocarbons having 7 or more carbon atoms, typically between 7 and 12 carbon atoms. Examples include heptane, heptene, octane, octene, toluene and the like.

The process of the invention can be used on any hydrocarbon feed stream containing olefins, particularly C₅ and / or C₆ components which can be separated into light and heavy fractions. In preferred embodiments, a catalytically or thermally cracked naphtha stream is the hydrocarbon feed stream, or fractions thereof. Such streams can be derived from any appropriate source, for example, they can be derived from the fluid catalytic cracking (FCC) of gas oils and resids, or from delayed or fluid coking of resids. In one embodiment the hydrocarbon feed streams used in the practice of the present invention is derived from the fluid catalytic cracking of gas oils and resids, and are typically rich in olefins and/or diolefins and relatively lean in paraffins.

Preferred catalytically cracked naphtha streams which are suitable for the practice of this invention include those streams or fractions thereof boiling in the naphtha range and containing from about 5 weight % to about 70 weight %, preferably from about 10 weight % to about 60 weight %, and more preferably from about 10 to 50 weight % paraffins, and from about 10 weight %, preferably from about 20 weight % to about 70 weight % olefins. The feed may also contain naphthenes and aromatics. Naphtha boiling range streams are typically those

boiling in the range from about 18°C to 22°C, and preferably from about 18°C to 149°C.

Catalysts

5 The catalysts that may be used in the practice of the invention include those which comprise a crystalline zeolite having an average pore diameter less than about 0.7 nanometers (nm), said crystalline zeolite comprising from about 10 weight % to about 50 weight % of the total fluidized catalyst composition. It is preferred that the crystalline zeolite be selected from the family of medium pore
10 size (< 0.7 nm) crystalline aluminosilicates, otherwise referred to as zeolites. The pore diameter also sometimes referred to as effective pore diameter can be measured using standard adsorption techniques and hydrocarbonaceous compounds of known minimum kinetic diameters. See Breck, *Zeolite Molecular Sieves*, 1974 and Anderson et al., *J. Catalysis* 58, 114 (1979).

15 Medium pore size zeolites that can be used in the practice of the present invention are described in "Atlas of Zeolite Structure Types", eds. W. H. Meier and D.H. Olson, Butterworth-Heineman, Third Edition, 1992. The medium pore size zeolites generally have a pore size from about 5Å, to about 7Å and include for example, MFI, MFS, MEL, MTW, EUO, MTT, HEU, FER, and TON
20 structure type zeolites (IUPAC Commission of Zeolite Nomenclature). Non-limiting examples of such medium pore size zeolites, include ZSM-5, ZSM-12, ZSM-22, ZSM-23, ZSM-34, ZSM-35, ZSM-38, ZSM-48, ZSM-50, and silicalite. The most preferred is ZSM-5, which is described in U.S. Patent Nos. 3,702,886 and 3,770,614. ZSM-11 is described in U.S. Patent No. 3,709,979; ZSM-12 in
25 U.S. Patent No. 3,832,449; ZSM-21 and ZSM-38 in U.S. Patent No. 3,948,758; ZSM-23 in U.S. Patent No. 4,076,842; and ZSM-35 in U.S. Patent No. 4,016,245.

 The medium pore size zeolites can include "crystalline admixtures" which are thought to be the result of faults occurring within the crystal or crystalline area during the synthesis of the zeolites. Examples of crystalline admixtures of ZSM-5
30 and ZSM-11 are disclosed in U.S. Patent No. 4,229,424. The crystalline admixtures are themselves medium pore size zeolites and are not to be confused

with physical admixtures of zeolites in which distinct crystals of crystallites of different zeolites are physically present in the same catalyst composite or hydrothermal reaction mixtures.

The catalysts of the present invention may be held together with an inorganic oxide matrix component. The inorganic oxide matrix component binds the catalyst components together so that the catalyst product is hard enough to survive interparticle and reactor wall collisions. The inorganic oxide matrix can be made from an inorganic oxide sol or gel which is dried to "glue" the catalyst components together. Preferably, the inorganic oxide matrix is not catalytically active and will be comprised of oxides of silicon and aluminum. It is also preferred that separate alumina phases be incorporated into the inorganic oxide matrix. Species of aluminum oxyhydroxides-g-alumina, boehmite, diaspora, and transitional aluminas such as α -alumina, β -alumina, χ -alumina, δ -alumina, ϵ -alumina, γ -alumina, and τ -alumina can be employed. Preferably, the alumina species is an aluminum trihydroxide such as gibbsite, bayerite, nordstrandite, or doyleite. The matrix material may also contain phosphorous or aluminum phosphate.

Preferred silicoaluminophosphate (SAPO) catalysts useful in the present invention have a three-dimensional microporous crystal framework structure of PO_2^+ , AlO_2^- and SiO_2 tetrahedral units, and whose essential empirical chemical composition on an anhydrous basis is: $m \text{R}:(\text{Si}[x]\text{Al}[y]\text{P}[z])\text{O}_2$ wherein "R" represents at least one organic templating agent present in the intracrystalline pore system: "m" represents the moles of "R" present per mole of $(\text{Si}[x]\text{Al}[y]\text{P}[z])\text{O}_2$ and has a value of from zero to 0.3, the maximum value in each case depending upon the molecular dimensions of the templating agent and the available void volume of the pore system of the particular silicoaluminophosphate species involved, "x", "y" and "z" represent the mole fractions of silicon, aluminum and phosphorus, respectively, present as tetrahedral oxides, representing the following values for "x", "y" and "z".

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Mole Fraction

	x	y	z
	0.01	0.47	0.52
	0.94	0.01	0.05
5	0.98	0.01	0.01
	0.39	0.60	0.01
	0.01	0.60	0.39

When synthesized in accordance with the process disclosed in U. S. Patent 4,440,871, the minimum value of "m" in the formula above is 0.02. In a preferred sub-class of the SAPOs useful in this invention, the values of "x", "y" and "z" in the formula above are set out in the following table:

Mole Fraction

	x	y	z
	0.02	0.49	0.49
15	0.25	0.37	0.38
	0.25	0.48	0.27
	0.13	0.60	0.27
	0.02	0.60	0.38

Preferred SAPO catalysts include SAPO-11, SAPO-17, SAPO-31, SAPO-34, SAPO-35, SAPO-41, and SAPO-44.

The catalysts suitable for use in the present invention include, in addition to the SAPO catalysts, the metal integrated aluminophosphates (MeAPO and ELAPO) and metal integrated silicoaluminophosphates (MeAPSO and ElAPSO). The MeAPO, MeAPSO, ElAPO, and ElAPSO families have additional elements included in their framework. For example, Me represents the elements Co, Fe, Mg, Mn, or Zn, and El represents the elements Li, Be, Ga, Ge, As, or Ti. Preferred catalysts include MeAPO-11, MeAPO-31, MeAPO-41, MeAPSO-11, MeAPSO-31, and MeAPSO-41, MeAPSO-46, ElAPO-11, ElAPO-31, ElAPO-41, ElAPSO-11, ElAPSO-31, and ElAPSO-41.

The non-zeolitic SAPO, MeAPO, MeAPSO, ElAPO and ElAPSO classes of microporous materials are further described in the "Atlas of Zeolite Structure Types" by W. M. Meier, D. H. Olson and C. Baerlocher (4th ed., Butterworths/Intl. Zeolite Assoc. (1996) and "Introduction to Zeolite Science and Practice", H. Van Bekkum, E.M. Flanigen and J.C. Jansen Eds., Elsevier, New York, (1991).).

Other suitable medium pore size molecular sieves include the silicoaluminophosphates (SAPO), such as SAPO-4 and SAPO-11 which is described in U.S. Patent No. 4,440,871; chromosilicates; gallium silicates; iron silicates; aluminum phosphates (ALPO), such as ALPO-11 described in U.S. Patent No. 4,310,440; titanium aluminosilicates (TASO), such as TASO-45 described in EP-A No. 229,295; boron silicates, described in U.S. Patent No. 4,254,297; titanium aluminophosphates (TAPO), such as TAPO-11 described in U.S. Patent No. 4,500,651; and iron aluminosilicates.

The selected catalysts may also include cations selected from the group consisting of cations of Group IIA, Group IIIA, Groups IIIB to VIIBB and rare earth cations selected from the group consisting of cerium, lanthanum, praseodymium, neodymium, promethium, samarium, europium, gadolinium, terbium, dysprosium, holmium, erbium, thulium, ytterbium, lutetium and mixtures thereof.

Other useful catalysts are described in U. S. Patent 5,675,050, International Application WO 91/18851, U. S. Patent 4,666,875, and U. S. Patent 4,842,714.

The Process

In the practice of the present invention, the hydrocarbon feed stream is separated into a light portion and a heavy portion which may be accomplished by conventional separation techniques such as a single flash or multiple flashes or by distillation or fractionation, prior to introduction to a reactor having the catalyst.

The reactor may be a fixed bed, a moving bed, a transfer line, a riser or fluidized bed reactor containing the catalyst.

The reactions are performed under conditions generally known in the art. For example, preferred conditions include a catalyst contacting temperature in the range of about 400°C to 750°C, more preferably in the range of 450°C to 700°C, most preferably in the range of 500°C to 650°C. The catalyst contacting process is preferably carried out at a weight hourly space velocity (WHSV) in the range of about 0.1 Hr⁻¹ to about 300 Hr⁻¹, more preferably in the range of about 1.0 Hr⁻¹ to about 250 Hr⁻¹, and most preferably in the range of about 10 Hr⁻¹ to about 100 Hr⁻¹. Pressure in the contact zone may be from 10-3040 kPa, preferably 101-304 kPa, most preferably about 101 kPa. The catalyst to feed (wt/wt) ratio is from about 3 to 12, preferably from about 4 to 10, where catalyst weight is total weight of the catalyst composite. In one embodiment, steam may be concurrently introduced with the feed stream into the reaction zone, with the steam comprising up to about 50 wt.% of the hydrocarbon feed or in the range of about 10 to 250 mol.%, preferably from about 25 to 150 mol.% steam to hydrocarbon. The feed residence time in the reaction zone is preferably less than about 10 seconds, for example from about 1 to 10 seconds.

In one embodiment, the light portion is introduced into the reactor at a point before the point where the heavy portion(s) of the feed stream is introduced into the reactor. This is illustrated in Figure 1. Preferably, the heavy portion of the feed stream is introduced into the reactor at a point that is at least 1/3 of the total length of the reaction chamber apart from the point where the light portion is introduced. More preferably, the heavy portion of the feed stream is introduced into the reactor at a point that is at least 1/2 of the total length of the reaction chamber apart from the point where the light portion is introduced. Even more preferably, the heavy portion of the feed stream is introduced into the reactor at a point that is 1/3 to 1/2 of the total length of the reactor chamber apart from the point where the light portion is introduced.

The multiple portions of the feed stream may be reacted with the same or different catalysts. In one embodiment they are reacted with the same catalyst(s). In a preferred embodiment the heavy and light portions of a naphtha feed are reacted

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over a medium pore silicoaluminophosphate catalyst such as SAPO-11, RE SAPO-11, SAPO-41, and/or RE SAPO-41.

In another embodiment the light and heavy portions are reacted with different catalysts. Preferably, in the practice of this invention the light portion of the hydrocarbon feed stream is reacted with silicoaluminophosphates, such as SAPO-11, SAPO-41, rare earth ion exchanged SAPO-11, and/or rare earth ion exchanged SAPO-41 while the heavy portion is reacted over medium pore crystalline aluminosilicate zeolites such as ZSM-5, ZSM-11, ZSM-23, ZSM-48 and/or ZSM-22.

In another embodiment the reactor is a staged bed reactor where the first staged bed comprises one or more medium pore crystalline aluminosilicate zeolite catalysts such as ZSM-5, ZSM-11, and/or ZSM-22, and the heavy portion of the feed stream is introduced into the reactor such that it will react with the zeolite catalyst, while the second staged bed comprises medium pore silicoaluminophosphate molecular sieve catalysts such as SAPO-11, SAPO-41, rare earth SAPO-11, and/or rare earth SAPO-41 and the lighter portion of the feed stream is introduced into the reactor such that it will react with the silicoaluminophosphate catalyst.

It is within the scope of this invention that the catalysts be precoked prior to introduction of feed in order to further improve the selectivity to propylene. It is also within the scope of this invention that an effective amount of single ring aromatics be fed to the reaction zone to also improve the selectivity of propylene vs. ethylene. The aromatics may be from an external source such as a reforming process unit or they may consist of heavy naphtha recycle product from the instant process.

The Product

The propylene produced herein preferably comprises at least 80 mole % propylene, preferably at least 95 mole%, more preferably 97 mole% based upon the total C₃ product produced.

The processes described herein produce product comprising at least 20 weight % propylene, preferably at least 25 weight % propylene, based upon the weight of the total product produced.

In another preferred embodiment, the process described herein is operated
5 in the absence of a superfractionator.

In another embodiment, this invention relates to a process of polymerizing propylene comprising obtaining propylene produced by the process described herein and thereafter contacting the propylene and optionally other olefins, with an olefin polymerization catalyst. In a preferred embodiment the olefin
10 polymerization catalyst may comprise one or more Ziegler-Natta catalysts, conventional-type transition metal catalyst, metallocene catalysts, chromium catalysts, or vanadium catalysts.

Examples:

15 In the examples below the reactions were preformed in a 50 cc fixed bed reactor operated under a controlled preosure of 6 psig (0.04 MPa). The feed rate was 0.36 g/min. The effluent stream was analyzed by on-line gas chromatography. A column having a length of 60m packed with a dual flame ionization detector (FID) Hewlett Packard Model 5880. In Examples 1, 2 and 3 a
20 diluent of steam was also fed into the reactor at a steam to hydrocarbon ratio of 0.2. In Examples 4, 5 and 6 a diluent of steam was fed into the reactor at a steam to hydrocarbon ratio of 1.5.

Example 1 (comparative)

25 In this example, a blend of model compounds consisting of 16.7wt% 1-pentene, 15.6wt% 1-hexene, 11.4wt% 1-heptene, 4.4 wt% 1-octene, 1.3wt% nonene, 1.0wt% 1-decene, 11.7wt% n-pentane, 11.5wt% n-hexane, 5.7wt% n-heptane, 5.0wt% n-octane, 2.5wt% n-nonane, 1.7wt% n-octane, 0.6wt% benzene, 2.8wt% toluene, and 8.1wt% mixed xylenes was prepared to simulate a refinery
30 light catalytically cracked naphtha. This simulated light cat naphtha was then cracked over a commercial ZSM-5 catalyst at 50 hr⁻¹ WHSV and 590° C with 0.2 steam/hydrocarbon.

As can be seen from Table 1, the propylene yield obtained in cracking the simulated light cat naphtha over the commercial ZSM-5 catalyst is 19.8wt% propylene at 95% purity level in the C₃ stream. Ethylene yield was 4.7wt%.

5 Example 2: (comparative)

In this example, the same blend of model compounds used in Example 1 was cracked over a rare earth SAPO-11 catalyst. As can be seen from Table 1, the propylene yield obtained in cracking of the simulated light cat naphtha over the rare earth ion exchanged SAPO-11 catalyst is 24.4wt% propylene at 95% purity
10 level in the C₃ stream. Ethylene yield was 5.1wt%.

Example 3:

In this example, a blend consisting of 60.0wt% 1-pentene and 40.0wt% n-pentane was prepared to simulate the C₅ cut of a refinery light cat naphtha.
15 Separately, a blend consisting of 21.8wt% 1-hexene, 15.9wt% 1-heptene, 6.2wt% 1-octene, 1.9wt% 1-nonene, 1.4wt% 1-decene, 16.1wt% n-hexane, 8.0wt% n-heptane, 7.0wt% n-octane, 3.5wt% nonane, 2.4wt% decane, 0.8wt% benzene, 3.9wt% toluene, and 11.3wt% mixed xylenes was prepared to simulate the C₆⁺ cut of the refinery light cat naphtha. This simulated C₅ cut and C₆⁺ cuts were cracked
20 separately over the same rare earth ion exchanged SAPO-11 of Example 2. The residence time in the second reaction was calculated to simulate the shortened residence time of a feed stream injected at a point further along the reactor than the injection point of the first fraction.

As can be seen from Table 1, propylene yield was 26.0wt% at 95% purity
25 level in the C₃ cut. Ethylene yield was improved to 8.6wt%. This example illustrates the benefit of splitting the feed and cracking the feed fractions separately over the cracking catalyst.

Example 4: (comparative)

30 In this example, a blend of model compounds consisting of 19.0 wt% 1-pentene, 20.4wt% 1-hexene, 15.1wt% 1-heptene, 1.1wt% 1-octene, 10.4wt% n-pentane, 14.7% n-hexane, 13.5wt% n-heptane, 1.4wt% n-octane, 1.1wt% benzene,

and 3.3wt% toluene was prepared to simulate another refinery light cat naphtha. This simulated light cat naphtha was then cracked over a commercial ZSM-5 catalyst at 7.2 hr^{-1} WHSV and 600°C with 1.5 steam/hydrocarbon.

As can be seen from Table 2, the propylene yield obtained in cracking of the simulated light cat naphtha over the commercial ZSM-5 catalyst is 28.4wt% propylene at 52.2wt% conversion. Ethylene yield was 7.1wt%. Butylene yield was 14.2wt%.

Example 5: (comparative)

In this example, the same blend of model compounds which was used in Example 4 was cracked over a SAPO-11 catalyst at a weight hourly space velocity of 3.1 hr^{-1} . As can be seen from Table 2, the propylene yield obtained in cracking of the simulated light cat naphtha over SAPO-11 catalyst is 30.8wt% at 52.1wt% conversion. Ethylene yield is 5.6wt%. Butylene yield was 12.9wt%.

Example 6:

In this example, a blend consisting of 30wt% 1-pentene, 32.0wt% 1-hexene, 16 wt% n-pentane, 22wt% n-hexane was prepared to simulate the C_5/C_6 cut of the refinery light cat naphtha used in Example 4. Separately, a blend consisting of 42.5wt% 1-heptene, 3.2wt% 1-octene, 38wt% n-heptane, 3.8wt% n-octane, 3.1wt% benzene, 9.2wt% toluene was prepared to simulate the C_7+ cut of the refinery light cat naphtha used in Example 4. This simulated C_5/C_6 cut was cracked over SAPO-11 and the C_7+ cut was cracked over ZSM-5 catalyst. The residence time in the second reaction was calculated to simulate the shortened residence time of a feed stream injected at a point further along the reactor than the injection point of the first fraction. The combined yields were calculated and tabulated in Table 2.

As can be seen from Table 2, propylene yield was 32.2wt% at 52.2wt% conversion. Ethylene yield was 7.3wt%. Butylene yield was reduced to 8.5wt%. This example illustrates the benefit of splitting the feed and cracking the feed fractions separately over two different catalysts.

Table 1

	Example 1	Example 2	Example 3
Conversion (wt%)	40.1	44.9	51.2
Ethylene (wt%)	4.7	5.1	8.6
Propylene (wt%)	19.8	24.4	26.0
Butylenes (wt%)	12.5	11.8	11.4
Light Sats (wt%)	3.0	3.6	5.2
C3 olefinicity	95.6	95.7	95.2

Table 2

	Example 4	Example 5	Example 6
Conversion (wt%)	52.2	52.1	55.5
ethylene (wt%)	7.1	5.6	7.3
propylene (wt%)	20.4	30.0	32.2
butylenes (wt%)	14.2	12.9	8.5
Light Sats (wt%)	2.4	2.8	4.1

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As is apparent from the foregoing general description and the specific embodiments, while forms of the invention have been illustrated and described, various modifications can be made without departing from the spirit and scope of the invention. Accordingly it is not intended that the invention be limited thereby.

Claims:

1. A process to produce propylene from a hydrocarbon feed stream comprising C₃'s and/or C₆'s comprising introducing the light portion of the feed
5 stream into a reactor containing one or more catalysts separately from the heavy portion of the feed stream, wherein the light portion of the feedstream comprises that portion of the feed stream that has a boiling point range of 120°C or less, and the heavy portion of the feed stream is that portion left over after the light portion is removed.
- 10 2. The process of claim 1 wherein the hydrocarbon feed stream is a naphtha feed stream having a boiling range of from about 18 °C to about 220 °C comprising from about 5 to about 70 weight % paraffins and from about 10 to about 70 weight % olefins
- 15 3. The process of claim 1 wherein the light portion of the feed stream comprises at least 75 weight% of the C₃'s and/or C₆'s present in the feed stream.
4. The process of claim 1 wherein the light portion of the feed stream
20 comprises at least 90 weight% of the C₃'s and/or C₆'s present in the feed stream.
5. The process of claim 1 wherein the light portion of the feed stream comprises at least 98 weight% of the C₃'s and/or C₆'s present in the feed stream.
- 25 6. The process of any of the preceding claims wherein the feedstream is a catalytically cracked naptha.
7. The process of any of the preceding claims wherein the feedstream is a thermally cracked naptha.

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8. The process of any of the preceding claims wherein the light portion is introduced into the reactor at a point before the point where the heavy portion of the hydrocarbon feed stream is introduced into the reactor.
- 5 9. The process of any of the preceding claims wherein the heavy portion of the feed stream is introduced into the reactor at a point that is at least $1/3$ of the total length of the reaction chamber apart from the point where the light portion is introduced.
- 10 10. The process of claim 8 wherein the heavy portion of the feed stream is introduced into the reactor at a point that is at least $1/2$ of the total length of the reaction chamber apart from the point where the light portion is introduced.
11. The process of claim 8 wherein the heavy portion of the feed stream is
15 introduced into the reactor at a point that is $1/3$ to $1/2$ of the total length of the reaction chamber apart from the point where the light portion is introduced.
12. The process of any of the preceding claims wherein the catalyst comprises a medium pore silicoaluminophosphate catalyst.
- 20 13. The process of any of the preceding claims wherein the catalyst comprises SAPO-11, RE SAPO-11, SAPO-41, and/or RE SAPO-41.
14. The process of any of the preceding claims wherein the reactor is a staged
25 bed reactor.
15. The process of claim 14 wherein the first staged bed comprises one or more medium pore aluminosilicate zeolite catalysts and the heavy portion of the feed stream is introduced into the reactor such that it will react with the zeolite
30 catalysts.



16. The process of claim 15 wherein the second staged bed comprises one or more silicoaluminophosphates, and the light portion is introduced into the reactor such that it will react with the silicoaluminophosphates.
- 5 17. The process of claim 15 wherein the zeolite catalyst is ZSM-5, ZSM-11, ZSM-23, ZSM-48 and/or ZSM-22.
18. The process of claim 16 wherein the silicoaluminophosphate is SAPO-11, RE SAPO-11, SAPO-41, and/or RE SAPO-41.
- 10 19. The process of claim 1 further comprising a second reactor wherein the light portion is introduced into a first reactor and the heavy portion of the feed stream is introduced into the second reactor.
- 15 20. The method of claim 19 wherein one or more silicoaluminophosphates are present in the first reactor.
21. The method of claim 19 wherein one or more medium pore aluminosilicate zeolites are present in the second reactor.
- 20 22. The method of claims 19-21 wherein the silicoaluminophosphate comprises one or more of SAPO-11, SAPO-41, RE SAPO-11, and RE-SAPO-41
23. The method of claims 19-21 wherein the zeolite comprises one or more of
- 25 ZSM-5, ZSM-11, ZSM-23, ZSM-48, and ZSM-22.
24. The process of any of the preceding claims wherein the process is operated in the absence of a superfractionator.
- 30 25. The process of any of the preceding claims wherein the product produced comprises at least 20 weight % propylene, based upon the weight of the total product produced.



26. The process of claim 1 or claims 3 through 25 wherein the hydrocarbon feed stream is a naphtha feed stream having a boiling range of from about 18 °C to about 220 °C.

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27. The process of claim 1 or claims 3 through 25 wherein the hydrocarbon feed stream is a naphtha feed stream having a boiling range of from about 18 °C to about 149 °C.

10 28. A process of polymerizing propylene comprising obtaining propylene produced by the process of any of the preceding claims and thereafter contacting the propylene, and optionally other olefins, with an olefin polymerization catalyst.

15 29. The process of any of the preceding claims wherein the olefin polymerization catalyst comprises one or more Ziegler-Natta catalysts, metallocene catalysts, chromium catalysts, or vanadium catalysts.

30. The process of any of the preceding claims wherein the light portion has a boiling point range of 100 °C or less.

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31. The process of any of the preceding claims wherein the light portion has a boiling point range of 80 °C or less.

