

PROCESS FOR THE CONVERSION OF LOWER ALKANES TO
ETHYLENE AND AROMATIC HYDROCARBONS

Field of the Invention

5 The present invention relates to an integrated process for producing ethylene and aromatic hydrocarbons from lower alkanes. More specifically, the invention relates to an integrated process for the production of ethylene and benzene from lower alkanes with lower capital and operating costs.

10 Background of the Invention

Ethylene and benzene are two of the most important basic products of the modern petrochemicals industry. Ethylene is used in the manufacture of other petrochemicals such as polyethylene, ethylene oxide, ethylene dichloride, and
15 ethylbenzene, among others. Benzene is used to make additional key petrochemicals such as styrene, phenol, nylon and polyurethanes, among others.

Ethylene is generally made from ethane and/or higher hydrocarbons in a high-temperature thermal or catalytic
20 cracker unit. The manufacture of olefins by hydrocarbon cracking is a well-established commercial process which is described in "Ethylene: Keystone to the Petrochemical Industry" by Ludwig Kniel, Marcel Dekker Publisher (1980).

When a feed of ethane plus one or more higher
25 hydrocarbons is converted into olefins in a cracker unit, it results in production of other olefins in addition to ethylene. These include propylene, butylenes, butadiene, pentenes, etc., depending on the composition of the cracker feedstock. The product separation scheme for such a mixed
30 feed cracker tends to be complicated by the presence of multiple olefin products which in many cases have to be separated from other similar molecules (such as the corresponding paraffins) to meet the product specifications. The end result is that the capital expenditure as well as the

operating costs of such a cracker complex are much higher than those of a cracker which produces only ethylene from a mainly ethane feedstock.

Generally, benzene and other aromatic hydrocarbons are
5 obtained by separating a feedstock fraction which is rich in aromatic compounds, such as reformates produced through a catalytic reforming process and pyrolysis gasolines produced through a naphtha cracking process, from non-aromatic hydrocarbons using a solvent extraction process. However, in
10 an effort to meet a projected aromatics supply shortage, numerous catalysts and processes for on-purpose production of aromatics (including benzene) from alkanes containing six or less carbon atoms per molecule have been investigated. The ease of conversion of individual alkanes to aromatics
15 increases with increasing carbon number and thus mixed alkane feeds have been considered. For example, U.S. 5,258,564 describes a process for converting C₂ to C₆ aliphatic hydrocarbons to aromatics comprising contacting the feed with a catalyst at dehydrocyclodimerization conditions wherein the
20 catalyst comprises a zeolite having a Si:Al ratio greater than 10 and a pore diameter of 5-6 Angstroms, a gallium component and an aluminum phosphate binder.

The catalysts used are usually bifunctional, containing a zeolite or molecular sieve material to provide acidity and
25 one or more metals such as Pt, Ga, Zn, Mo, etc. to provide dehydrogenation activity. For example, U.S. Patent 4,350,835 describes a process for converting ethane-containing gaseous feeds to aromatics using a crystalline zeolite catalyst of the ZSM-5-type family containing a minor amount of Ga. As
30 another example, U.S. Patent 7,186,871 describes aromatization of C₁-C₄ alkanes using a catalyst containing Pt and ZSM-5.

It would be advantageous to provide a lower alkane dehydroaromatization process wherein (a) lower cost ethylene can be produced as a coproduct and (b) the feed to the dehydroaromatization reactor is substantially all converted, thus avoiding any feed recycle and resulting in lower capital and operating costs.

Summary of the Invention

The present invention provides an integrated process for producing ethylene and aromatic hydrocarbons, specifically benzene, which comprises:

- (a) introducing a mixed lower alkane feed into an alkane cracker, preferably a thermal or catalytic cracker, to produce to produce a product mixture which is comprised of ethylene and C₃₊ products and possibly unreacted ethane,
- (b) separating and recovering ethylene,
- (c) contacting the C₃₊ products and any unreacted ethane with an aromatic hydrocarbon conversion catalyst to produce a product mixture which is comprised of aromatic reaction products including benzene, and
- (d) recovering benzene and any other aromatic reaction products.

In another embodiment, benzene may be separated from toluene and/or xylene, and C₉₊ aromatic products in step (c) and the benzene may be recovered. The toluene and/or xylene may then be hydrodealkylated to produce additional benzene.

Brief Description of the Drawings

Fig. 1 is a flow diagram which illustrates the once-through cracking of a mixed ethane/propane/butane stream to produce ethylene and other products which are separated and then converted into aromatics.

Fig. 2 is a flow diagram which illustrates the production of ethylene and other products which are separated and then converted into aromatics wherein benzene is

separated from toluene and xylene which are hydrodealkylated to produce more benzene.

Detailed Description of the Invention

This invention relates to an integrated processing
5 scheme for producing ethylene and benzene (and other
aromatics) from a mixed lower alkane stream which may contain
 C_2 , C_3 , C_4 and/or C_5 alkanes (referred to herein as "mixed
lower alkanes" or "lower alkanes"), for example an
ethane/propane/butane-rich stream derived from natural gas,
10 refinery or petrochemical streams including waste streams.
Examples of potentially suitable feed streams include (but
are not limited to) residual ethane and propane from natural
gas (methane) purification, pure ethane, propane and butane
streams (also known as Natural Gas Liquids) co-produced at a
15 liquefied natural gas site, C_2 - C_5 streams from associated
gases co-produced with crude oil production, unreacted ethane
"waste" streams from steam crackers, and the C_1 - C_3 byproduct
stream from naphtha reformers. The lower alkane feed may be
deliberately diluted with relatively inert gases such as
20 nitrogen and/or with various light hydrocarbons and/or with
low levels of additives needed to improve catalyst
performance. The primary desired products of the process of
this invention are ethylene, benzene, toluene and xylene.

The hydrocarbons in the feedstock may include ethane,
25 propane, butane, and/or C_5 alkanes or any combination
thereof. Preferably, the majority of the lower alkanes in
the feedstock is ethane and propane. The feedstock may
contain in addition other open chain hydrocarbons containing
between 3 and 8 carbon atoms as coreactants. Specific
30 examples of such additional coreactants are propylene,
isobutane, n-butenes and isobutene. The hydrocarbon
feedstock preferably is comprised of at least about 30

percent by weight of C₂₋₄ hydrocarbons, preferably at least about 50 percent by weight.

The integrated process may involve first producing ethylene from such a lower alkane-rich feedstock in a
5 cracker, preferably a catalytic or thermal cracker. However, the cracker is designed in such a manner that only ethylene is recovered as the desired product and no provision is made to separate and recover other olefins or diolefins co-produced such as propylene, butenes, butadiene, etc.
10 Further, the cracker design is simplified in that there is no recycle of unconverted feed including ethane, propane, etc. Following a product separation scheme to recover ethylene and methane/hydrogen (as light ends), the remaining C₂₊ stream is sent to the aromatization step, which may be a catalytic
15 alkanes-to-benzene reaction, to produce benzene and other aromatics. In this manner, the benzene unit functions as a means of converting essentially all C₃₊ hydrocarbons from the feedstock going to the ethane cracker--as well as most of the unreacted ethane from the cracker--into aromatics, thus
20 simplifying its design considerably. An advantage of this invention is that the capital and operating cost of the ethane cracker complex is significantly reduced by eliminating recovery of propylene and other olefins. In addition, the benzene process also is operated in a high-
25 conversion, single-pass manner with no recycle of unconverted feed, resulting in further capital and operating cost reduction for the overall integrated processing scheme described.

Lower olefins, i.e. ethylene and propylene, may be
30 produced from lower alkanes (ethane, propane and butane) by either thermal or catalytic cracking processes. The thermal cracking process may typically be carried out in the presence of superheated steam and this is by far the most common

commercially practiced process. Steam cracking is a thermal cracking process in which saturated hydrocarbons (i.e. ethane, propane, butane or their mixture) are broken down into smaller, unsaturated hydrocarbons, i.e, olefins and
5 hydrogen.

In steam cracking, the gaseous feed may be diluted with steam and then briefly heated in a furnace (without the presence of oxygen). Typically, the reaction temperature may be very high – around 750 to 950°C – but the reaction is only
10 allowed to take place very briefly. In modern cracking furnaces, the residence time may even be reduced to milliseconds (resulting in gas velocities reaching speeds beyond the speed of sound) in order to improve the yield of desired products. After the cracking temperature has been
15 reached, the gas may quickly be quenched to stop the reaction in a transfer line heat exchanger.

The products produced in the reaction depend on the composition of the feed, the hydrocarbon to steam ratio and on the cracking temperature and furnace residence time. The
20 process may typically be operated at low pressures, around 140 to 500 kPa depending on the overall process design.

The process may also result in the slow deposition of coke, a form of carbon, on the reactor walls. This degrades the efficiency of the reactor so reaction conditions are
25 designed to minimize this. Nonetheless, a steam cracking furnace can usually only run for a few months at a time between de-cokings. De-cokings require the furnace to be isolated from the process and then a flow of steam or a steam/air mixture is passed through the furnace coils at high
30 temperature. This converts the hard solid carbon layer to carbon monoxide and carbon dioxide. Once this reaction is complete, the furnace can be returned to service.

In many commercial operations, ethylene and propylene are separated from the resulting complex mixture by repeated compression and distillation at low temperatures. In the process of the present invention, only ethylene is separated
5 from the product.

The first stages of olefin production and purification in a cracker complex are: 1) steam cracking in furnaces as described above; 2) primary and secondary heat recovery with quench; 3) dilution steam recycle between the furnaces and
10 the quench system; 4) primary compression of the cracked gas (multiple stages of compression); 5) hydrogen sulfide and carbon dioxide removal (acid gas removal); 6) secondary compression (1 or 2 stages); 7) drying of the cracked gas; and 8) cryogenic treatment of the dried, cracked gas.

15 The cold, cracked gas stream is then treated in a demethanizer. The overhead stream from the demethanizer, consisting of hydrogen and methane, is treated cryogenically to separate the hydrogen and methane. This separation step usually involves liquid methane at a temperature of about -
20 150°C. Complete recovery of all the methane is critical to the economical operation of the olefin plant.

The bottom stream from the demethanizer tower is treated in a deethanizer tower. The overhead stream from the deethanizer tower consists of all the C₂'s that were in the
25 cracked gas stream. The C₂'s then go to a C₂ splitter. The product ethylene is taken from the overhead of the tower and the ethane coming from the bottom of the splitter is recycled to the furnaces to be cracked again.

The bottom stream from the deethanizer tower may go to a
30 depropanizer tower but is preferably eliminated in the process of this invention. The overhead stream from the depropanizer tower consists of all the C₃'s that were in the cracked gas stream. Prior to sending the C₃'s to the C₃

splitter this stream is hydrogenated in order to react out the methylacetylene and propadiene. Then this stream is sent to the C₃ splitter. The overhead stream from the C₃ splitter is product propylene and the bottom stream from the C₃ splitter is propane which can be sent back to the furnaces for cracking or used as fuel.

The bottom stream from the depropanizer tower may go to a debutanizer tower but this is preferably eliminated in the process of this invention. The overhead stream from the debutanizer is all of the C₄'s that are in the cracked gas stream. The bottom stream from the debutanizer consists of everything in the cracked gas stream that is C₅ or heavier. This could be called a light pyrolysis gasoline.

Since the production of ethylene is energy intensive, much effort has been dedicated recovering heat from the gas leaving the furnaces. Most of the energy recovered from the cracked gas may be used to make high pressure (around 8300 kPa) steam. This steam may in turn be used to drive the turbines for compressing cracked gas and the ethylene refrigeration compressor.

The ethylene manufacturing process may also accomplished by in the presence of a catalyst. The advantages are the use of much lower temperatures and possibly the absence of steam. In principle, a higher selectivity to olefins and possibly lower coke make can be achieved. Though it has not been practiced commercially at a world scale plant, catalytic cracking of ethane has been an area of interest for a long time. The types of catalysts used to crack higher hydrocarbons include zeolites, clays, aluminosilicates, and others. It should be mentioned that this process is practiced commercially in several oil refineries for high molecular weight hydrocarbons which are cracked over zeolite catalysts in a process unit called FCC (Fluidized Catalytic

Cracker). It is more common in such processes to produce and recover propylene as a byproduct rather than both ethylene and propylene.

The second step of the integrated process comprises
5 catalytic production of benzene from the mixed unconverted lower alkane and C₃₊ olefin-containing output from the cracker during which substantially all of C₃₊ hydrocarbons and most of the ethane are converted in a single pass. In one embodiment, at least 90% by weight of propane and heavier
10 hydrocarbons in the feed to this step is converted to aromatic hydrocarbons and byproducts, preferably at least 95% by weight and most preferably at least 99% by weight. The reaction may take place in the presence of a catalyst composition suitable for promoting the reaction of lower
15 alkanes to aromatic hydrocarbons such as benzene. The reaction conditions may comprise a temperature of 550 to 750°C and a pressure of 0.01 to 0.5 Mpa absolute.

Any one of a variety of catalysts may be used to promote the reaction of lower alkanes to aromatic hydrocarbons. One
20 such catalyst is described in U.S. 4,899,006. The catalyst composition described therein comprises an aluminosilicate having gallium deposited thereon and/or an aluminosilicate in which cations have been exchanged with gallium ions. The molar ratio of silica to alumina is at least 5:1.

25 Another catalyst which may be used in the process of the present invention is described in EP 0 244 162. This catalyst comprises the catalyst described in the preceding paragraph and a Group VIII metal selected from rhodium and platinum. The aluminosilicates are said to preferably be MFI
30 or MEL type structures and may be ZSM-5, ZSM-8, ZSM-11, ZSM-12 or ZSM-35.

Other catalysts which may be used in the process of the present invention are described in U.S. 7,186,871 and U.S.

7,186,872. The first of these patents describes a platinum containing ZSM-5 crystalline zeolite synthesized by preparing the zeolite containing the aluminum and silicon in the framework, depositing platinum on the zeolite and calcining the zeolite. The second patent describes such a catalyst which contains gallium in the framework and is essentially aluminum-free.

Additional catalysts which may be used in the process of the present invention include those described in U.S. 5,227,557. These catalysts contain an MFI zeolite plus at least one noble metal from the platinum family and at least one additional metal chosen from the group consisting of tin, germanium, lead, and indium.

One preferred catalyst for use in this invention is described in U.S. Provisional Application No. 61/029481, filed February 18, 2008 entitled "Process for the Conversion of Ethane to Aromatic Hydrocarbons" (now U. S. application No. 12/371787, filed February 16, 2009). This application describes a catalyst comprising: (1) 0.005 to 0.1 %wt (% by weight) platinum, based on the metal, preferably 0.01 to 0.05 %wt, (2) an amount of an attenuating metal selected from the group consisting of tin, lead, and germanium, which is no more than 0.02 %wt less than the amount of platinum, preferably not more than 0.2 %wt of the catalyst, based on the metal; (3) 10 to 99.9 %wt of an aluminosilicate, preferably a zeolite, based on the aluminosilicate, preferably 30 to 99.9 %wt, preferably selected from the group consisting of ZSM-5, ZSM-11, ZSM-12, ZSM-23, or ZSM-35, preferably converted to the H⁺ form, preferably having a SiO₂/Al₂O₃ molar ratio of from 20:1 to 80:1, and (4) a binder, preferably selected from silica, alumina and mixtures thereof.

Another preferred catalyst for use in this invention is described in U.S. Provisional Application No. 61/029939, filed February 20, 2008 entitled "Process for the Conversion of Ethane to Aromatic Hydrocarbons" (now PCT/US2009/034364, 5 filed February 18, 2009). The application describes a catalyst comprising: (1) 0.005 to 0.1 %wt (% by weight) platinum, based on the metal, preferably 0.01 to 0.06 %wt, most preferably 0.01 to 0.05 %wt, (2) an amount of iron which is equal to or greater than the amount of the platinum but 10 not more than 0.50 %wt of the catalyst, preferably not more than 0.20 %wt of the catalyst, most preferably not more than 0.10 %wt of the catalyst, based on the metal; (3) 10 to 99.9 %wt of an aluminosilicate, preferably a zeolite, based on the aluminosilicate, preferably 30 to 99.9 %wt, preferably 15 selected from the group consisting of ZSM-5, ZSM-11, ZSM-12, ZSM-23, or ZSM-35, preferably converted to the H⁺ form, preferably having a SiO₂/Al₂O₃ molar ratio of from 20:1 to 80:1, and (4) a binder, preferably selected from silica, alumina and mixtures thereof.

20 Another preferred catalyst for use in this invention is described in U.S. Provisional Application No. 61/029478, filed February 18, 2008 entitled "Process for the Conversion of Ethane to Aromatic Hydrocarbons" (now U. S. application No. 12/371803, filed February 16, 2009). This application 25 describes a catalyst comprising: (1) 0.005 to 0.1 wt% (% by weight) platinum, based on the metal, preferably 0.01 to 0.05% wt, most preferably 0.02 to 0.05% wt, (2) an amount of gallium which is equal to or greater than the amount of the platinum, preferably no more than 1 wt%, most preferably no 30 more than 0.5 wt%, based on the metal; (3) 10 to 99.9 wt% of an aluminosilicate, preferably a zeolite, based on the aluminosilicate, preferably 30 to 99.9 wt%, preferably selected from the group consisting of ZSM-5, ZSM-11, ZSM-12,

ZSM-23, or ZSM-35, preferably converted to the H⁺ form, preferably having a SiO₂/Al₂O₃ molar ratio of from 20:1 to 80:1, and (4) a binder, preferably selected from silica, alumina and mixtures thereof.

5 The hydrodealkylation reaction involves the reaction of toluene, xylenes, ethylbenzene, and higher aromatics with hydrogen to strip alkyl groups from the aromatic ring to produce additional benzene and light ends including methane and ethane which are separated from the benzene. This step
10 substantially increases the overall yield of benzene and thus is highly advantageous.

 Both thermal and catalytic hydrodealkylation processes are known in the art. Thermal dealkylation may be carried out as described in U.S. 4,806,700. Hydrodealkylation
15 operation temperatures in the described thermal process may range from 500 to 800°C at the inlet to the hydrodealkylation reactor. The pressure may range from 2000 kPa to 7000 kPa. A liquid hourly space velocity in the range of 0.5 to 5.0 based upon available internal volume of the reaction vessel
20 may be utilized.

 Due to the exothermic nature of the reaction, it is often required to perform the reaction in two or more stages with intermediate cooling or quenching of the reactants. Two or three or more reaction vessels may therefore be used in
25 series. The cooling may be achieved by indirect heat exchange or interstage cooling. When two reaction vessels are employed in the hydrodealkylation zone, it is preferred that the first reaction vessel be essentially devoid of any internal structure and that the second vessel contain
30 sufficient internal structure to promote plug flow of the reactants through a portion of the vessel.

 Alternatively, the hydrodealkylation zone may contain a bed of a solid catalyst such as the catalyst described in

U.S. 3,751,503. Another possible catalytic hydrodealkylation process is described in U.S. 6,635,792, which is herein incorporated by reference in its entirety. This patent describes a hydrodealkylation process carried out over a
5 zeolite-containing catalyst which also contains platinum and tin or lead. The process is preferentially performed at temperatures ranging from 250 °C to 600 °C, pressures ranging from 0.5 MPa to 5.0 MPa, liquid hydrocarbon feed rates from 0.5 to 10 hr⁻¹ weight hourly space velocity, and molar
10 hydrogen/hydrocarbon feedstock ratios ranging from 0.5 to 10.

One embodiment of the concept of this invention is illustrated in the simplified block flow diagram in Figure 1. In Figure 1, the ethane/propane/butane-rich stream 2 is fed to an olefin cracker 4 which may be operated in a once-
15 through manner. In separation section 6, only ethylene 8 is recovered and light ends 10 (mainly methane and H₂) are separated from the remaining product stream 12, which consists of unreacted feed (ethane/propane/butane etc.) and other co-products such as propylene, butene, etc. This feed
20 stream 12 in turn is sent to the alkane to benzene reactor 14 which contains a suitable catalyst or catalyst mixture. Light ends (mainly methane and H₂) are separated in line 18. The reactor product stream 16 contains unreacted ethane and diluent (if any), plus small amounts of C₃-C₅ hydrocarbons,
25 benzene, toluene, xylenes and heavier aromatics, with selectivity to benzene preferably greater than 20%. This product stream 16 passes through appropriate separation and extraction equipment (not shown) to separate the aromatics from the unreacted ethane which may be recycled to the ethane
30 cracker. The H₂ may be optionally recovered (but not necessarily) from the C₁ (methane) streams 10 and/or 18 using pressure swing adsorption or a membrane process and sent to a hydrodealkylation unit as described below.

There are several variations to the process, the main objective of which is to produce ethylene and aromatics from a single mixed feedstock 2 containing ethane and higher hydrocarbons. In one version, as shown in Figure 1, only the produced benzene is recovered. There is no hydrodealkylation unit and the toluene and xylenes co-produced are recovered along with the C₉₊ aromatics. In another version, as shown in Figure 2, both toluene and xylenes are selectively converted into benzene and methane. This additional benzene is then added to the benzene produced in the main reaction. In another variation (not shown), no attempt is made to separate the benzene, toluene, and xylene components and their mixture is sent to the hydrodealkylation unit.

In the embodiment described in Figure 2, the hydrogen from the light ends streams 10 and/or 18 may be introduced into a hydrodealkylation unit after separation of the methane as described above. The aromatics stream 16 is directed to separation unit 20 in which the benzene is separated from toluene and xylene. Benzene leaves separation unit 20 through line 22. Toluene and xylene leave separation unit 20 through line 24 and are directed to the hydrodealkylation unit 26 in which the toluene and xylene are converted into benzene 28 which is then combined with benzene stream 22. The C₉₊ aromatics leave separation unit 20 through line 30. A light ends stream 31 may also leave separation unit 20.

EXAMPLES

The examples provided below are intended to illustrate but not limit the scope of the invention.

Example 1

Catalysts A and B were made with low levels of Pt and Ga on extrudate samples containing 80%wt of CBV 2314 ZSM-5 powder (23:1 molar $\text{SiO}_2\text{:Al}_2\text{O}_3$ ratio, available from Zeolyst International) and 20%wt alumina binder. These catalysts were prepared as described in U.S. Provisional Application No. 61/029478, filed February 18, 2008 entitled "Process for the Conversion of Ethane to Aromatic Hydrocarbons." The extrudate samples were calcined in air up to 650°C to remove residual moisture prior to use in catalyst preparation. The target metal loadings for catalyst A were 0.025%w Pt and 0.09%wt Ga. The target metal loadings for catalyst B were 0.025%wt Pt and 0.15%wt Ga.

Metals were deposited on 25-50 gram samples of the above ZSM-5/alumina extrudate by first combining appropriate amounts of stock aqueous solutions of tetraammine platinum nitrate and gallium(III) nitrate, diluting this mixture with deionized water to a volume just sufficient to fill the pores of the extrudate, and impregnating the extrudate with this solution at room temperature and atmospheric pressure. Impregnated samples were aged at room temperature for 2-3 hours and then dried overnight at 100°C.

Catalysts made on the ZSM-5/alumina extrudate were tested "as is," without crushing. For each performance test, a 15-cc charge of fresh (not previously tested) catalyst was loaded into a Type 316H stainless steel tube (1.40 cm i.d.) and positioned in a four-zone furnace connected to a gas flow system.

Prior to performance testing, the catalyst charges were pretreated in situ at atmospheric pressure (ca. 0.1 MPa absolute) as follows:

- (a) calcination with air at 60 liters per hour (L/hr), during which the reactor wall temperature was increased from 25 to 510°C in 12 hrs, held at 510°C

for 4-8 hrs, then further increased from 510 to 630°C in 1 hr, then held at 630°C for 30 min;

(b) nitrogen purge at 60 L/hr, 630°C for 20 min;

(c) reduction with hydrogen at 60 L/hr, for 30 min,

5 during which time the reactor wall temperature was raised from 630°C to the temperature used for the actual run.

At the end of the above reduction step, the hydrogen flow was terminated, and the catalyst charge was exposed to a feed
10 consisting of 67.2%wt ethane and 32.8%wt propane at atmospheric pressure (ca. 0.1 MPa absolute), 650-700°C reactor wall temperature, and a feed rate of 500-1000 GHSV (500-1000 cc feed per cc catalyst per hr). Three minutes after introduction of the feed, the total reactor outlet stream was
15 sampled by an online gas chromatograph for analysis. Based on composition data obtained from the gas chromatographic analysis, initial ethane, propane and total conversions were computed according to the following formulas:

ethane conversion, % = $100 \times (\% \text{wt ethane in feed} - \% \text{wt ethane in outlet stream}) / (\% \text{wt ethane in feed})$
20

propane conversion, % = $100 \times (\% \text{wt propane in feed} - \% \text{wt propane in outlet stream}) / (\% \text{wt propane in feed})$

total ethane + propane conversion = $((\% \text{wt ethane in feed} \times \% \text{ethane conversion}) + (\% \text{wt propane in feed} \times \% \text{propane conversion})) / 100$
25

Table 1 lists the results of online gas chromatographic analyses of samples of the total product streams of these reactors taken at 3 minutes after introduction of the feed. Under these conditions, over 99%wt of the propane in the feed
30 and over 55%w of the ethane in the feed was converted in all of these catalyst performance tests. The product stream contains benzene and higher aromatics, along with hydrogen and light hydrocarbons, including some ethane which can be recycled.

TH3521-PCT

TABLE 1

Catalyst	A	B	B	A	B	A
Catalyst charge weight, g	11.58	11.52	12.36	11.43	11.51	11.73
Reactor Wall Temperature, °C						
Total feed rate, GHSV	650	675	675	700	700	700
Total feed rate, WHSV	500	600	1000	800	800	1000
	0.89	1.07	1.67	1.44	1.43	1.76
% Ethane Conversion	56.38	71.07	58.22	77.16	77.05	65.77
% Propane Conversion	99.3	99.48	99.11	99.61	99.61	99.5
Total % (Ethane + Propane) Conversion	70.51	80.4	71.64	84.53	84.45	76.84
Reactor Outlet Composition, %wt						
Hydrogen	5.31	6.29	5.71	6.48	6.54	5.99
Methane	17.91	19.28	16.36	20.47	20.25	17.13
Ethylene	2.11	3.83	2.89	5.76	5.45	6.65
Ethane	29.26	19.43	28.06	15.34	15.42	22.99
Propylene	0.22	0.33	0.32	0.46	0.43	0.67
Propane	0.23	0.17	0.29	0.13	0.13	0.16
C4	0.02	0.02	0.03	0.05	0.05	0.09
C5	0	0	0	0	0	0
Benzene	26.97	29.68	27.45	30.06	30.34	24.99
Toluene	8.15	8.28	8.21	7.97	7.92	8.09
C8 Aromatics	0.74	0.83	0.79	0.94	0.88	1.06
C9+ Aromatics	9.06	11.86	9.88	12.33	12.58	12.17
Total Aromatics	44.93	50.84	46.33	51.31	51.73	46.31

Example 2

Using fresh (not previously tested) charges of catalysts A and B described in Example 1 additional performance tests were conducted as described in Example 1 except that the feed
5 consisted of 32.8%w ethane and 67.2%w propane. Table 2 lists the results of online gas chromatographic analyses of samples of the total product streams of these reactors taken at 3 minutes after introduction of the feed. Under these conditions, over 99%wt of the propane in the feed and over
10 20%w of the ethane in the feed was converted in all of these catalyst performance tests. The product stream contains benzene and higher aromatics, along with hydrogen and light hydrocarbons, including some ethane which can be recycled.

15

TH3521-PCT

TABLE 2

Catalyst	A	B	B	B	B	A
Catalyst charge weight, g	11.58	11.51	11.52	11.93	12.36	11.73
Reactor Wall Temperature, °C						
Total feed rate, GHSV	650	675	675	675	675	700
Total feed rate, WHSV	500	500	600	800	1000	800
	0.99	0.98	1.22	1.57	1.9	1.6
% Ethane Conversion	23.73	59.12	48.81	42.53	36.17	66.32
% Propane Conversion	99.65	99.84	99.78	99.74	99.68	99.85
Total % (Ethane + Propane) Conversion	74.55	86.38	83.09	81	78.88	88.86
Reactor Outlet Composition, %wt						
Hydrogen	4.79	5.7	5.45	5.61	5.78	5.78
Methane	19.65	23.7	22.34	19.64	17.05	24.54
Ethylene	2.88	2.95	3.1	3.67	4.17	4.44
Ethane	25.21	13.51	16.77	18.83	20.91	11.03
Propylene	0.27	0.21	0.27	0.38	0.45	0.37
Propane	0.23	0.11	0.14	0.17	0.21	0.1
C4	0.03	0.01	0.02	0.05	0.06	0.04
C5	0	0	0	0	0	0
Benzene	27.23	31.73	30.71	29.14	26.99	29.44
Toluene	9.28	7.75	8.77	9.82	10.17	7.69
C8 Aromatics	1.08	0.71	0.9	1.19	1.4	0.91
C9+ Aromatics	9.34	13.61	11.52	11.51	12.82	15.66
Total Aromatics	46.93	53.8	51.9	51.65	51.37	53.69

C L A I M S

1. An integrated process for producing ethylene and aromatic hydrocarbons which comprises:

- 5 (a) introducing a mixed lower alkane feed into an alkane cracker, preferably a thermal or catalytic cracker, to produce a product mixture which is comprised of ethylene and C₃₊ products and possibly unreacted ethane,
- (b) separating and recovering ethylene,
- 10 (c) contacting the C₃₊ products and any unreacted ethane with an aromatic hydrocarbon conversion catalyst to produce aromatic reaction products including benzene, and
- (d) recovering benzene and any other aromatic reaction products.

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2. The process of claim 1 wherein the majority of the lower alkanes in the mixed lower alkane feed is comprised of ethane and propane.

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3. The process of claims 1 or 2 wherein the mixed lower alkane feed is comprised of at least 30 percent by weight of C₂₋₄ hydrocarbons, preferably at least 50 percent by weight.

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4. An integrated process for producing ethylene and aromatic hydrocarbons which comprises:

- (a) introducing a mixed lower alkane feed into an alkane thermal or catalytic cracker, preferably a thermal or catalytic cracker, to produce a product mixture which is
- 30 comprised of ethylene and C₃₊ products and possibly unreacted ethane,
- (b) separating and recovering ethylene,

(c) contacting the C₃₊ products and any unreacted ethane with an aromatic hydrocarbon conversion catalyst to produce a product mixture which is comprised of benzene and toluene and/or xylene, and C₉₊ aromatic products,

5 (d) separating and recovering the aromatic reaction products,

(e) separating benzene from the other aromatic reaction products and recovering the benzene, and

(f) hydrodealkylating toluene and/or xylene to produce
10 additional benzene.

5. The process of claim 4 wherein the majority of the lower alkanes in the mixed lower alkane feed is comprised of ethane and propane.

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6. The process of claims 4 or 5 wherein the mixed lower alkane feed is comprised of at least 30 percent by weight of C₂₋₄ hydrocarbons, preferably at least 50 percent by weight.

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