

(51) International Patent Classification:
C07C 2/00 (2006.01)77084 (US). MADGAVKAR, Ajay Madhav [US/US];
3102 Bentgrass Drive, Katy, Texas 77450 (US).(21) International Application Number:
PCT/US2011/031917(74) Agent: CARRUTH, James D.; Shell Oil Company, One
Shell Plaza, P.O. Box 2463, Houston, Texas 77252-2463
(US).(22) International Filing Date:
11 April 2011 (11.04.2011)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
61/323,017 12 April 2010 (12.04.2010) US(71) Applicant (for SM only): SHELL OIL COMPANY
[US/US]; One Shell Plaza, P.O. Box 2463, Houston,
Texas 77252-2463 (US).(71) Applicant (for all designated States except US): SHELL
INTERNATIONALE RESEARCH MAATSCHAPPIJ
B.V. [NL/NL]; Carel van Bylandtlaan 30, NL-2596 The
Hague (NL).

(72) Inventors; and

(75) Inventors/Applicants (for US only): JOIS, Yajna-
narayana Halmuthur [US/US]; 1910 Brookchester
Drive, Katy, Texas 77450 (US). LAURITZEN, Ann
Marie [US/US]; 16810 Gaelic Lane, Houston, Texas(81) Designated States (unless otherwise indicated, for every
kind of national protection available): AE, AG, AL, AM,
AO, AT, AU, AZ, BA, BB, BG, BH, BR, BW, BY, BZ,
CA, CH, CL, CN, CO, CR, CU, CZ, DE, DK, DM, DO,
DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT,
HN, HR, HU, ID, IL, IN, IS, JP, KE, KG, KM, KN, KP,
KR, KZ, LA, LC, LK, LR, LS, LT, LU, LY, MA, MD,
ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI,
NO, NZ, OM, PE, PG, PH, PL, PT, RO, RS, RU, SC, SD,
SE, SG, SK, SL, SM, ST, SV, SY, TH, TJ, TM, TN, TR,
TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.(84) Designated States (unless otherwise indicated, for every
kind of regional protection available): ARIPO (BW, GH,
GM, KE, LR, LS, MW, MZ, NA, SD, SL, SZ, TZ, UG,
ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, MD, RU, TJ,
TM), European (AL, AT, BE, BG, CH, CY, CZ, DE, DK,
EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU,
LV, MC, MK, MT, NL, NO, PL, PT, RO, RS, SE, SI, SK,
SM, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ,
GW, ML, MR, NE, SN, TD, TG).

[Continued on next page]

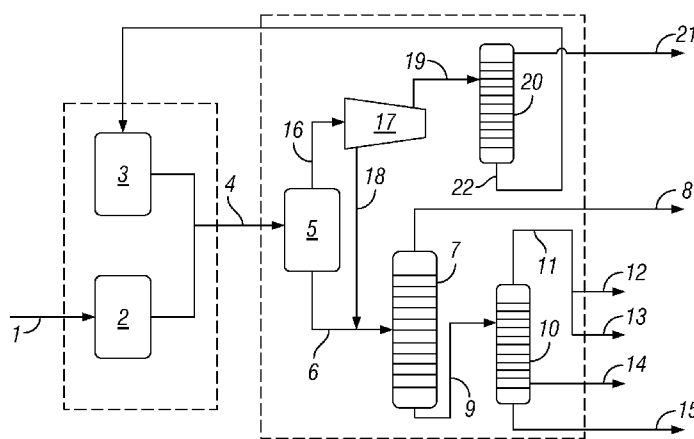
(54) Title: PROCESS FOR THE PRODUCTION OF GASOLINE BLENDING COMPONENTS AND AROMATIC HYDRO-
CARBONS FROM LOWER ALKANES

FIG. 1

(57) Abstract: An integrated process for
producing gasoline blending components
and aromatic hydrocarbons which compris-
es: (a) contacting a lower alkane feed with
an aromatic hydrocarbon conversion cata-
lyst to produce an aromatic reaction prod-
uct mixture which is comprised of benzene and/
or toluene and/or xylene, C₉ aromatic prod-
ucts, C₁₀ aromatic products including naph-
thalene and, optionally, C₁₁₊ aromatic prod-
ucts, (b) separating and recovering the aro-
matic reaction product mixture, (c) separat-
ing and recovering benzene, (d) optionall-
ly separating recovering toluene and/or xy-
lene, and (e) separating and recovering the
C₉ aromatic products and the C₁₀ aromatic
products which boil at a lower temperature
than naphthalene from the naphthalene and
the C₁₀ aromatic reaction products which
boil at a higher temperature than naphtha-
lene and any C₁₁₊ aromatic products.



Published:

— with international search report (Art. 21(3))

— before the expiration of the time limit for amending the claims and to be republished in the event of receipt of amendments (Rule 48.2(h))

PROCESS FOR THE PRODUCTION OF GASOLINE
BLENDING COMPONENTS AND AROMATIC
HYDROCARBONS FROM LOWER ALKANES

5 Field of the Invention

The present invention relates to a process for producing gasoline blending components and aromatic hydrocarbons from lower alkanes. The invention also relates to a novel gasoline blending component.

10 Background of the Invention

There is a projected global shortage for benzene which is generally obtained, along with other aromatic hydrocarbons, by separating a feedstock fraction which is rich in aromatic compounds, such as reformate produced through a catalytic reforming process and pyrolysis gasolines produced through a naphtha cracking process, from non-aromatic hydrocarbons using a solvent extraction process. To meet this projected 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. 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 another example, U.S. Patent 7,186,871 describes aromatization of C₁-C₄ alkanes using a catalyst containing Pt and ZSM-5.

It is well known to add certain blending components to gasolines to improve the properties thereof such as the RON or the MON. Commonly used blending components include naphthas (e.g., straight-run gasoline, alkylate, reformate, toluene, xylene), cracked gasoline, pyrolysis gasoline, and paraffinic hydrocarbons.

U.S. Patent No. 6,353,143 describes fuel compositions which are comprised of a branched hydrocarbon, such as an isoparaffin, and an aromatic hydrocarbon. An example of a suitable aromatic hydrocarbon given is AROMATIC 150 Fluid from Exxon Chemical which typically is composed of a narrow-cut aromatic solvent containing about 23 wt. % tetra-methyl benzenes, about 22 wt. % ethyl dimethyl benzenes, about 15 wt. % mono-, di- and tri-methyl indanes, about 8 wt. % diethyl benzenes, about 8 wt. % naphthalene, about 5 wt. % trimethyl benzenes, about 2 wt. % indane, and about 1 wt. % or less of methyl ethyl benzenes, propyl benzenes, methyl propyl benzenes, butyl benzenes, hexyl benzenes, indene, methyl naphthalenes, and xylenes. Another example of an aromatic hydrocarbon given is AROMMATIC 100 which typically is composed of a narrow-cut aromatic solvent containing about 40 wt. % trimethyl benzenes, about 35 wt. % methyl ethyl benzenes, about 1 wt. % propyl and isopropyl benzenes, about 3 wt.% ethyl dimethyl benzenes, about 2 wt. % methyl (n- and iso-) propyl benzenes, about 2 wt. % diethyl benzenes, less than about 1 wt. % each of mono butyl benzenes and tetramethyl benzenes, about 6 wt. % xylenes, and minor amounts of ethyl benzene and C₁₀ -C₁₁ saturates.

Summary of the Invention

The present invention provides an integrated process for producing gasoline blending components and aromatic hydrocarbons which comprises:

(a) contacting a lower alkane feed with an aromatic hydrocarbon conversion catalyst to produce an aromatic reaction product mixture which is comprised of benzene and/or toluene and/or xylene, C₉ aromatic products, C₁₀ aromatic products including naphthalene and, optionally, C₁₁₊ aromatic products,

(b) separating and recovering the aromatic reaction product mixture,

(c) separating and recovering benzene, and

(d) separating and recovering toluene and/or xylene and the C₉ aromatic products and the C₁₀ aromatic products which boil at a lower temperature than naphthalene from the naphthalene and the C₁₀ aromatic reaction products which boil at a higher temperature than naphthalene and any C₁₁₊ aromatic products.

10 Brief Description of the Drawings

Fig. 1 is a flow diagram of a two stage aromatization process wherein benzene, toluene and/or xylene and the C₉₋₁₀ fraction are recovered separately.

15 Fig. 2 is a flow diagram of a two stage aromatization process wherein the process also comprises hydrodealkylation of the toluene and xylene to make additional benzene.

Fig. 3 is a flow diagram of the two stage aromatization process wherein the C₉₋₁₀ fraction is recovered together with the toluene and xylene as a single gasoline blending
20 component.

Detailed Description of the Invention

Gasolines typically comprise mixtures of hydrocarbons boiling in the range from 25 to 230 °C (EN-ISO 3405), the optimal ranges and distillation curves typically varying
25 according to climate and season of the year. The hydrocarbons in a gasoline may be derived by any means known in the art, conveniently the hydrocarbons may be derived in any known manner from straight-run gasoline, synthetically-produced aromatic hydrocarbon mixtures, thermally or
30 catalytically cracked hydrocarbons, hydro-cracked petroleum fractions, catalytically reformed hydrocarbons or mixtures of these.

The specific distillation curve, hydrocarbon composition, research octane number (RON) and motor octane number (MON) of the gasoline are not critical. Conveniently, the research octane number (RON) of the gasoline may be at
5 least 80, for instance in the range of from 80 to 110 (EN 25164). The motor octane number (MON) of the gasoline may conveniently be at least 70, for instance in the range of from 70 to 110 (EN 25163).

Gasoline is composed of many different hydrocarbons.
10 Typically, gasoline comprises components selected from one or more of the following groups; saturated hydrocarbons, olefinic hydrocarbons, aromatic hydrocarbons, and oxygenated hydrocarbons. Typically, the aromatic hydrocarbon content of the gasoline may be in the range of from 0 to 70 percent by
15 volume based on the gasoline (ASTM D1319).

Crude oil enters a refinery and is processed through various units before being blended into gasoline. A refinery may have a fluid catalytic cracker (FCC), an alkylate unit, and a reformer, each of which produces gasoline blending
20 components. Alkylate gasoline, for example, is valuable because it has a very high octane, and can be used to produce high-octane (and higher value) blends. Light straight run gasoline is the least processed stream. It is cheap to produce, but it has a low octane. The person specifying the
25 gasoline blends has to mix all of the components together to meet the product specifications.

It is well known to add certain blending components to gasoline to improve the properties thereof such as the RON or the MON. Commonly used blending components include naphthas
30 (e.g., straight-run gasoline, alkylate, reformate, benzene, toluene, xylene), cracked gasoline, pyrolysis gasoline, and paraffinic hydrocarbons. The present invention provides a novel gasoline blending component which comprises from about

1 to 10 wt% indane, from about 40 to 60% wt indene, from about 4 to 20 wt% C₉ aromatics other than indane or indene, and from about 25 to 35 wt% C₁₀ aromatics other than naphthalene.

5 The process of the present invention comprises bringing into contact a hydrocarbon feedstock containing lower alkanes, and possibly other hydrocarbons, and a catalyst composition suitable for promoting the reaction of such hydrocarbons to aromatic hydrocarbons, such as benzene, at a
10 temperature from about 400 to about 700°C and a pressure from about 0.01 to about 1.0 Mpa absolute. The gas hourly space velocity (GHSV) per hour may range from about 300 to about 6000. The process may be carried out in a single stage or in multiple, preferably two, stages. If a two-stage process is
15 used, the conditions in each stage may fall in the above ranges and may be the same or different.

 Suitable feed streams for use herein include alkane streams which may contain primarily one or more C₂, C₃, and/or C₄ alkanes (referred to herein as "lower alkanes"),
20 for example an ethane/propane/butane-rich stream derived from natural gas, 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
25 and butane streams (also known as Natural Gas Liquids) co-produced at a liquefied natural gas site, C₂-C₅ streams from associated gases co-produced with crude oil production, unreacted ethane "waste" streams from steam crackers, and the C₁-C₃ byproduct stream from naphtha reformers. The lower
30 alkane feed may be deliberately diluted with relatively inert gases such as nitrogen and/or with various light hydrocarbons and/or with low levels of additives needed to improve catalyst performance.

In one embodiment, the majority of the feedstock is comprised of ethane and propane. In another embodiment, the feedstock is comprised of mixed C₂-C₄ alkanes. In still another embodiment, the feedstock is comprised of primarily propane and butane. The feedstock may contain in addition other open chain hydrocarbons containing between 3 and 8 carbon atoms as coreactants. Specific examples of such additional coreactants are propylene, isobutane, n-butenes and isobutene. The feed may contain up to about 20 weight percent of C₂-C₄ olefins, preferably no more than about 10 weight percent olefins. Too much olefin content may cause an unacceptable amount of coking. The hydrocarbon feedstock preferably may be comprised of at least about 30 percent by weight of C₂₋₄ hydrocarbons, preferably at least about 50 percent by weight.

In one embodiment, the lower alkane feed is comprised of at least propane and ethane and the process is carried out in two stages as described in copending, commonly assigned provisional U.S. patent application number 61/257085, entitled PROCESS FOR THE CONVERSION MIXED LOWER ALKANES TO AROMATIC HYDROCARBONS, filed November 2, 2009, which is herein incorporated by reference in its entirety. In the first stage, the reaction conditions may be optimized for the conversion of propane to benzene. In the second stage, reaction conditions may be optimized for the conversion of ethane to benzene. Optionally, the second stage reaction conditions may also be optimized for the conversion to BTX of any other non-aromatic hydrocarbons which may be produced in the first stage.

In another embodiment, as described in copending, commonly assigned provisional U.S. patent application number 61/257149, entitled PROCESS FOR THE CONVERSION LOWER ALKANES TO AROMATIC HYDROCARBONS, filed November 2, 2009, which is

herein incorporated by reference in its entirety, the process (a) comprises alternately contacting the lower alkane feed with an aromatization catalyst in a reactor for a short period of time, preferably 10 minutes or less, and then
5 contacting the aromatization catalyst with hydrogen at elevated temperature for a short period of time, preferably 20 minutes or less, (b) repeating the cycle of step (a) at least one time, (c) regenerating the aromatization catalyst by contacting it with an oxygen-containing gas at elevated
10 temperature, and (d) repeating steps (a) through (c) at least one time.

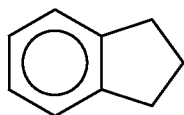
One important advantage of the aromatization process used herein is that little or no C₅₊ non-aromatic hydrocarbons are produced. The C₁₋₄ non-aromatic hydrocarbons
15 which are produced may be recycled or used for fuel, etc. The major products produced are aromatic. Benzene, and generally toluene and xylene, are recovered, leaving a substantial amount of C₉₊ aromatic hydrocarbons. We have discovered that a significant portion of the C₉₊ fraction
20 produced from lower alkanes in this aromatization process may be used as a gasoline-blending component with attractive properties. Accordingly, a product separation scheme is incorporated in the aromatization process to efficiently separate and recover the desirable portion of the C₉₊ mixture
25 so that a maximum amount of desirable gasoline blending component is obtained. The C₉₊ fraction includes naphthalene and higher boiling C₁₀₊ aromatic hydrocarbons which are not useful for gasoline blending components because its boiling range is higher than specified/typical gasoline range.

30 In the present invention, the C₉ aromatic hydrocarbons and the C₁₀ aromatic hydrocarbons which boil at lower temperatures than naphthalene are recovered separately. The C₉ aromatic hydrocarbons include indane, indene, durene,

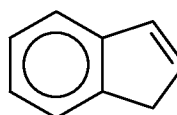
propylbenzene, etc. and the lower boiling C₁₀ aromatic hydrocarbons include methylindane, methylindene, methylpropylbenzene, butylbenzene, diethylbenzene, etc. The combined C₉ aromatic hydrocarbons and C₁₀ aromatic hydrocarbons which boil at lower temperatures than naphthalene comprise the gasoline blending component of the present invention. It may comprise from about 1 to 10 wt% indane, from about 40 to 60 wt% indene, from about 4 to 20 wt% C₉ aromatics other than indane or indene, and from about 25 to 35 wt% C₁₀ aromatics other than naphthalene.

Indane is a hydrocarbon petrochemical compound with chemical formula C₉H₁₀. Derivatives include compounds such as 1-methyl-indane and 2-methyl-indane (where one methyl group is attached to the five carbon ring), 4-methyl-indane and 5-methyl-indane (where one methyl group is attached to the benzene ring), various dimethyl-indanes, and various pharmaceutical derivatives. Indene is an unsaturated polycyclic hydrocarbon with chemical formula C₉H₈. It is composed of a benzene ring fused with a cyclopentene ring.

Multiple chemical analyses of the C₉₊ fraction obtained experimentally show that indane and indene form the majority of the C₉ molecules while methyl substituted indane and indene and naphthalene form the majority of the C₁₀ molecules. Indane and indene



Indane



Indene

are similar in structure to benzene, ethyl benzene and propyl benzene which are known to have high octane and high flame speed boosting properties as shown in Table 1.

Table 1

Compound	RON	MON	Flame Speed	b.p. °C
----------	-----	-----	-------------	---------

			cm/sec	
Benzene	105	99	84	80.1
Toluene	120	109	67.9	110.6
Isooctane	100	100	67	98.5
Ethylbenzene	111.2	97.9	76.9	136.2
1,2,4 Trimethylbenzene (Pseudocumene)	110.5	105.8	58.3	169.4
1,3,5 Trimethylbenzene (Mesitylene)	120.3	120.3	56	164.7
isopropylbenzene	113.1	99.3	76.3	152.4
n-propylbenzene			74.1	
t-butylbenzene			75.7	

Fig. 1 is a flow diagram of a two stage aromatization process wherein a C₉₋₁₀ only fraction is recovered. Lower alkane feed enters stage 1 aromatization reactor 2 through line 1. The reaction products are combined with the reaction products from stage 2 aromatization reactor 3 in line 4 which is conveyed to a vapor-liquid separator 5. The liquid bottoms leave the separator 5 in line 6 and are conveyed to the debenzenizer 7 wherein benzene is separated from the other aromatic products and is recovered in line 8. The other aromatic products in the bottom stream 9 are conveyed to the toluene-xylene-C₉₋₁₀ separation stage 10. The toluene and xylene leave separation stage 10 through line 11 and are recovered separately as toluene in line 12 and xylene in line 13. The C₉₋₁₀ fraction is taken out of separation stage 10 and recovered in line 14. The remaining C₉₋₁₀₊ aromatics leave stage 10 through line 15.

Vapor stream 16 leaves separator 5 and is compressed in compressor 17. Any aromatics carried over to the compressor are conveyed to the debenzenizer 7 through line 18. The other liquids are conveyed through line 19 to demethanizer 20 wherein the methane and hydrogen are separated and recovered as fuel gas in line 21. The bottom stream 22 of the demethanizer 20 contains C₂₋₄ hydrocarbons which are recycled to the second stage aromatization reactor 3.

Fig. 2 is a flow diagram of the two stage aromatization process wherein the process scheme of Fig. 1 includes at the

end a hydrodealkylation section wherein the toluene and xylene are reacted to produce more benzene. Most of the process description is the same as for Fig. 1. Instead of being separated, the toluene and xylene in line 11 are conveyed to a hydrodealkylation unit 26 which produces additional benzene in line 28 and some fuel gas components in line 29. Unreacted toluene and xylene are recycled to the debenzenizer through line 27. The overhead stream 21 from demethanizer 20 is conveyed to separator 23 which separates hydrogen from other fuel gas components. The hydrogen is conveyed through line 25 to the hydrodealkylation unit 26. The remaining fuel gas components from separator 23 are combined with line 29 and recovered as fuel gas through line 24.

Fig. 3 is a flow diagram of a two stage aromatization process wherein the C₉₋₁₀ fraction is recovered together with the toluene and xylene as a single gasoline blending component. In this embodiment, the toluene, xylene and the C₉₋₁₀ fractions are not recovered separately but are recovered together as a combined gasoline blending component in line 11.

Any one of a variety of catalysts may be used to promote the reaction of the lower alkanes to aromatic hydrocarbons. One such catalyst is described in U.S. 4,899,006 which is herein incorporated by reference in its entirety. 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.

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 or MEL type structures and may be ZSM-5, ZSM-8, ZSM-11, ZSM-12 or ZSM-35.

5 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, both of which are herein incorporated by reference in their entirety. The first of these patents describes a platinum containing ZSM-5 crystalline zeolite synthesized by
10 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.

15 Additional catalysts which may be used in the process of the present invention include those described in U.S. 5,227,557, hereby incorporated by reference in its entirety. These catalysts contain an MFI zeolite plus at least one noble metal from the platinum family and at least one
20 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. Patent Application Publication No. 2009/0209795. This publication is hereby incorporated by
25 reference in its entirety. This publication 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
30 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 PCT Publication No. WO 2009/105447. This publication is hereby incorporated by reference in its entirety. The publication 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 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 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. Patent Application Publication No.

2009/0209794. This publication is hereby incorporated by reference in its entirety. This publication 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 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.

The unreacted methane and byproduct hydrocarbons may be used in other steps, stored and/or recycled. It may be necessary to cool these byproducts to liquefy them. When the ethane or mixed lower alkanes originate from an LNG plant as a result of the purification of the natural gas, at least some of these byproducts may be cooled and liquefied using the heat exchangers used to liquefy the purified natural gas (methane).

The toluene and xylene may be converted into benzene by hydrodealkylation. 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 substantially increases the overall yield of benzene and thus is highly advantageous.

Both thermal and catalytic hydrodealkylation processes are known in the art. Methods for hydrodealkylation are described in U.S. Patent Application Publication No. 2009/0156870 which is herein incorporated by reference in its entirety.

The integrated process of this invention may also include the reaction of benzene with propylene to produce cumene which may in turn be converted into phenol and/or acetone. The propylene may be produced separately in a propane dehydrogenation unit or may come from olefin cracker

process vent streams or other sources. Methods for the reaction of benzene with propylene to produce cumene are described in U.S. Patent Application Publication No. 2009/0156870 which is herein incorporated by reference in its entirety.

The integrated process of this invention may also include the reaction of benzene with olefins such as ethylene. The ethylene may be produced separately in an ethane dehydrogenation unit or may come from olefin cracker process vent streams or other sources. Ethylbenzene is an organic chemical compound which is an aromatic hydrocarbon. Its major use is in the petrochemical industry as an intermediate compound for the production of styrene, which in turn is used for making polystyrene, a commonly used plastic material. Methods for the reaction of benzene with ethylene to produce ethylbenzene are described in U.S. Patent Application Publication No. 2009/0156870 which is herein incorporated by reference in its entirety.

Styrene may then be produced by dehydrogenating the ethylbenzene. One process for producing styrene is described in U.S. Pat. No. 4,857,498 which is herein incorporated by reference in its entirety. Another process for producing styrene is described in U.S. Pat. No. 7,276,636 which is herein incorporated by reference in its entirety.

EXAMPLES

The following examples are provided for illustrative purposes only and are not intended to limit the scope of the invention.

Example 1

Indane and indene were obtained from vendors. Toluene was used as a benchmark in this study of the fuel blending

properties. The RON and MON of neat indane, indene, toluene, and a base fuel were tested using ASTM D-2699 and ASTM D-2700 test method. All compounds were tested in triplicate and the average of those results were presented in Table 2. The RON and MON of the base fuel and toluene were reasonably high as expected and the RON and MON of indane and indene were also reasonable high.

Table 2

Neat					
Density		Average			delta
g/ml		RON	MON	R + M/2	R-M
0.743	Base Fuel	85.4	79.0	82.1	6.5
0.865	Toluene	114.5	106.0	110.3	8.5
0.965	Indane	100.7	85.5	93.1	15.2
0.996	Indene	108.0	98.5	103.2	9.5

The RON and MON of 1.2 v% indane and indene in base fuel blends were measured (see the top part of Table 3). The RON and MON of 3.7v% toluene, 4.7 v% indane and 4.6 v% indene in base fuel blends were also measured (see the bottom part of Table 3). Table 3 below shows an increase in Research Octane Number of 0.43 and 0.5 with 1.2v% of indane and indene, respectively. Table 3 shows an increase in Research Octane Number of 0.90 and 0.80 with 4.7v% of indane and 4.6 v% indene, respectively.

Table 3

		Average			delta		
Density (g/ml)		RON	MON	R+M/2	RON	MON	R+M/2
0.743	Base Fuel (BF)	86.3	79.8	83.0			
0.965	Indane (1.2 v% in BF)	86.7	79.8	83.2	0.43	-0.03	0.2
0.996	Indene (1.2 v%)	86.8	79.5	83.1	0.50	-0.30	0.1
		Average			delta		
Density (g/ml)		RON	MON	R+M/2	RON	MON	R+M/2
0.743	Base Fuel	86.67	79.83	83.3			
0.865	Toluene (3.7 v%)	87.6	80.23	83.9	0.93	0.40	0.7
0.965	Indane (4.7 v%)	87.57	80.23	83.9	0.90	0.40	0.6
0.996	Indene (4.6 v%)	87.47	79.57	83.5	0.80	-0.27	0.2

Such increase in octane number is known in the literature for aromatic molecules. However, it is generally compensated for by a decrease in flame speed. The flame speeds of above molecules were measured using the Leeds University bomb experiment technique at Leeds University facility. Fuel samples were tested under laminar conditions with initial conditions of 5 bar absolute pressure and 360K. All the burning velocities (flame speed) were measured at stoichiometric ratio of fuel to air. The experiments were conducted using the Leeds Mk2 fan stirred combustion vessel (Refer to www.engineering.leeds.ac.uk/mech for their facility). It is a stainless sphere of 30 liter volume with extensive optical access. The fuels were injected into the bomb and allowed to vaporize fully, then a stoichiometric amount of air was added. Content were heated to the desired temperature, mixed by stirring. Mixing fans were turned off prior to ignition. Pressure measured after 0.1 second of the ignition is recorded in Table 4. To determine if there was any significant change due to the presence of a component, it was decided to do experiments using 20v% of the components in commercial grade gasoline. No significant change in flame speed was noted for indane or indene as shown in Table 4. The data in Tables 1-4 indicate that indane, indene, other C₉

aromatics, and certain C₁₀ aromatics other than naphthalene would comprise suitable gasoline blending components.

Table 4

5

Flame Speed Data		
Molecule	Blend Composition	Flame Speed
	% in Gasoline	P/bar at 0.1 Second
Gasoline	100	17.35
Indane	20	17.24
Indene	20	16.10

Example 2

Four runs were carried out in a lab-scale aromatization reactor at 0 kPag, 600°C reactor wall temperature with repeated cycles of 10 minute exposure of the catalyst to feed followed by 20 minute exposure of the catalyst to hot hydrogen stripping. The feed and other conditions are described in Table 5 below. The catalysts used in these runs were prepared as described in U.S. Patent Application Publication No. 2009/02009794, which is incorporated by reference, with target metal loadings of 0.025 wt% platinum and 0.09 wt% gallium or 0.09 wt% platinum and 0.25 wt% gallium, on extrudates consisting of 80 wt% ZSM-5 CBV 2314 zeolite (available from Zeolyst International) and 20 wt% alumina binder. A gas chromatograph was used to provide quantitative analysis of the total product stream.

As shown in Table 5, the total C₉₊ aromatics fraction accounted for about 8-15wt% of the total aromatics product in runs conducted with all-ethane and mixed ethane/propane feeds. The C₉₋₁₀ aromatics fraction excluding naphthalene ranged between about 45 and 60%w of the total C₉₊ aromatics product or about 4-8%w of the total aromatics product in these runs.

30

Table 5

Run No.	1	2	3	4
Feed Composition				
Ethane, %wt	100	100	50	50
Propane, %wt	-0-	-0-	50	50
Feed Rate, GHSV	800	800	1000	1000
Total Hrs on Feed	14.4	50.7	27.2	50.7
Avg Total C2 + C3 Conversion per Pass, %	38.40	33.66	47.26	47.06
Avg Total Arom. Yield per Pass, %wt	23.57	20.01	30.19	32.81
Avg C9+ Arom. Yield per Pass, %wt	3.29	2.61	3.30	2.95
Avg C9-C10 Arom. (Except Naphthalene)				
Yield as % of C9+ Aromatics	45.3	59.8	56.7	48.5
Yield as % of Total Aromatics	6.3	7.8	6.2	4.4
Avg Naphthalene and Higher Aromatics				
Yield as % of C9+ Aromatics	54.7	40.2	43.3	51.5
Yield as % of Total Aromatics	7.6	5.2	4.7	4.6
Final Boiling Point of Collected Liquid Product, °C	NA	493	NA	453

C L A I M S

1. An integrated process for producing gasoline
blending components and aromatic hydrocarbons which

5 comprises:

(a) contacting a lower alkane feed with an aromatic
hydrocarbon conversion catalyst to produce an aromatic
reaction product mixture which is comprised of benzene and/or
toluene and/or xylene, C₉ aromatic products, C₁₀ aromatic
10 products including naphthalene and, optionally, C₁₁₊ aromatic
products,

(b) separating and recovering the aromatic reaction
product mixture,

(c) separating and recovering benzene, and

15 (d) separating and recovering toluene and/or xylene and
the C₉ aromatic products and the C₁₀ aromatic products which
boil at a lower temperature than naphthalene from the
naphthalene and the C₁₀ aromatic reaction products which boil
at a higher temperature than naphthalene and any C₁₁₊ aromatic
20 products.

2. A process as claimed in claim 1 wherein step (d)
further comprises separating and recovering toluene and/or
xylene and separating and recovering the C₉ aromatic products
and the C₁₀ aromatic products which boil at a lower
25 temperature than naphthalene.

3. A process as claimed in claim 1 further comprising
hydrodealkylating the toluene and/or xylene to produce
additional benzene.

4. A process as claimed in claim 1 wherein the C₉
30 aromatic products and the C₁₀ aromatic products which boil at
a lower temperature than naphthalene comprises indane, methyl
indane, indene, methyl indene or mixtures thereof.

5. A gasoline blending component which comprises a component selected from the group consisting of indane, methyl indane, indene, methyl indene and mixtures thereof.

5 4. The gasoline blending component of claim 5 which further comprises toluene and/or xylene.

5. The gasoline blending component of claim 5 which comprises from about 1 to 10 wt% indane, from about 40 to 60
10 wt% indene, from about 4 to 20 wt% C₉ aromatics other than indane or indene, and from about 25 to 35 wt% C₁₀ aromatics other than naphthalene.

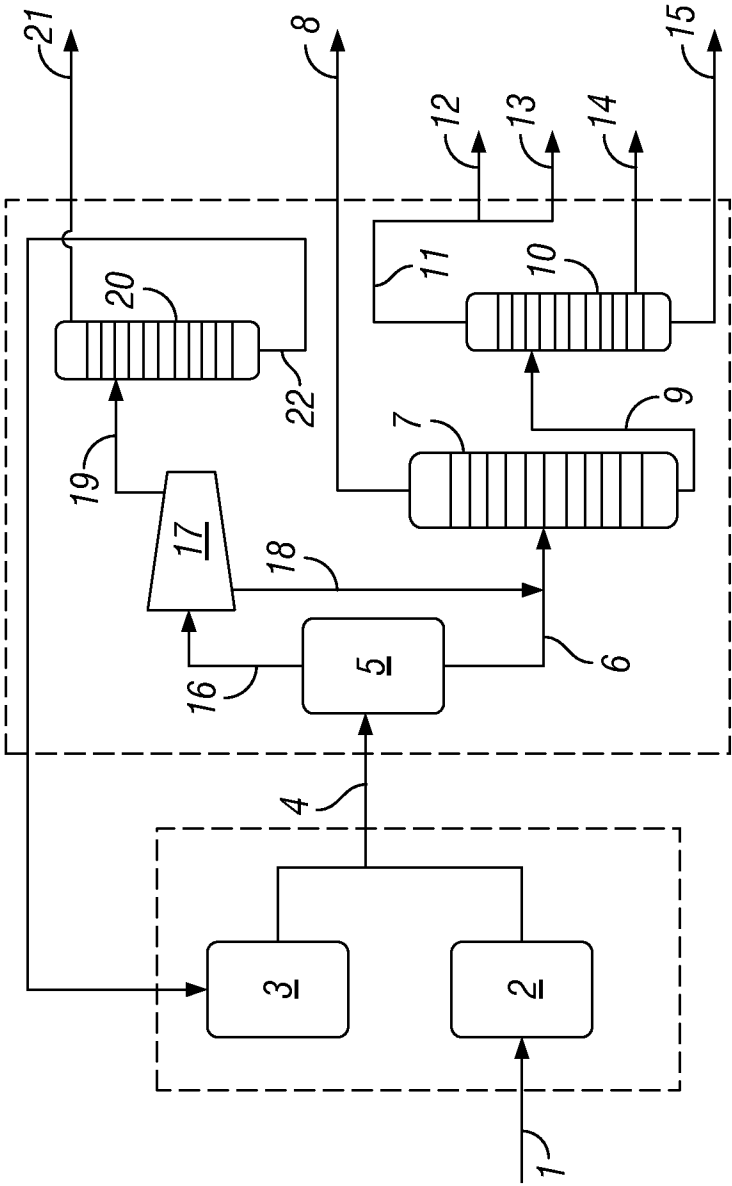


FIG. 1

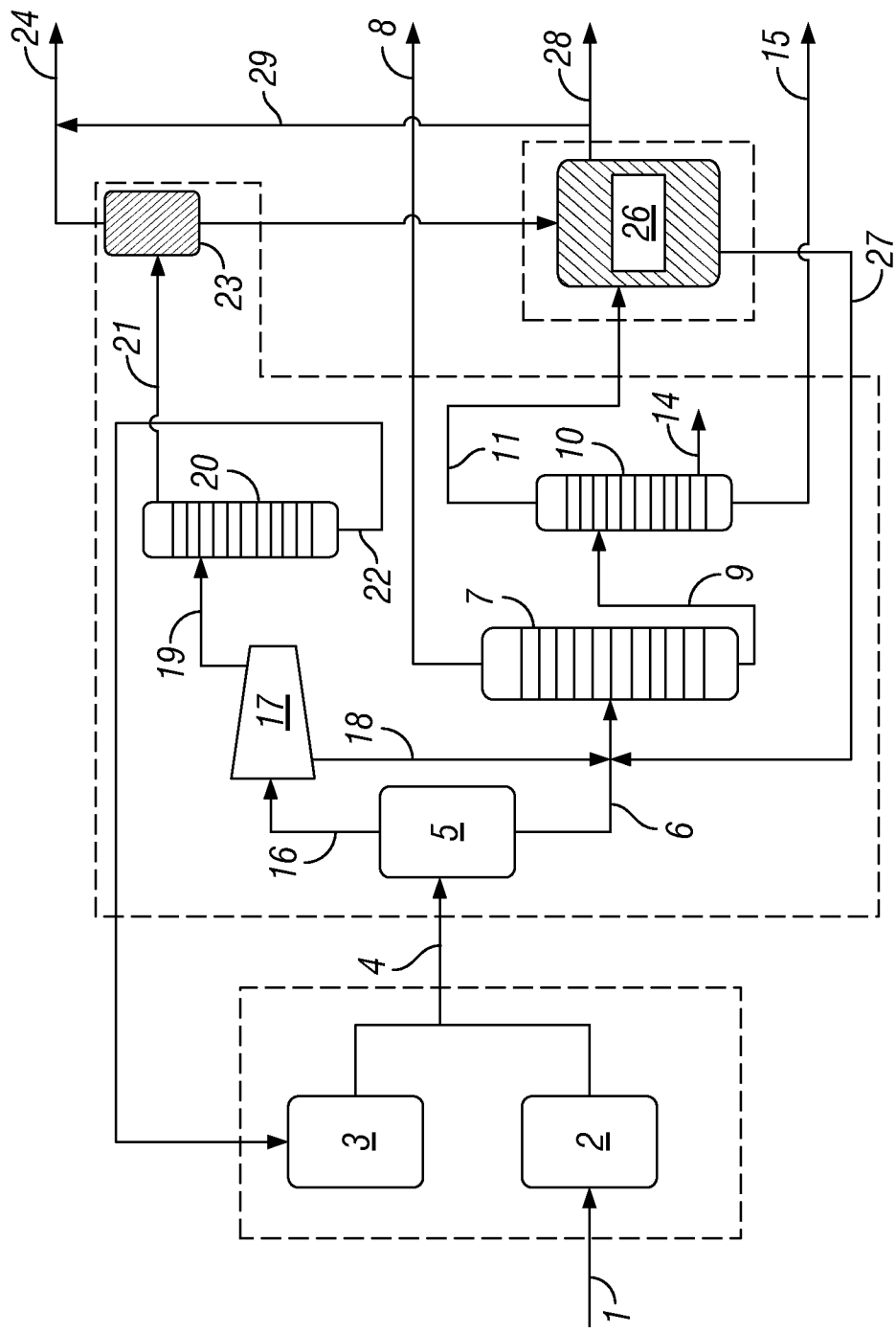


FIG. 2

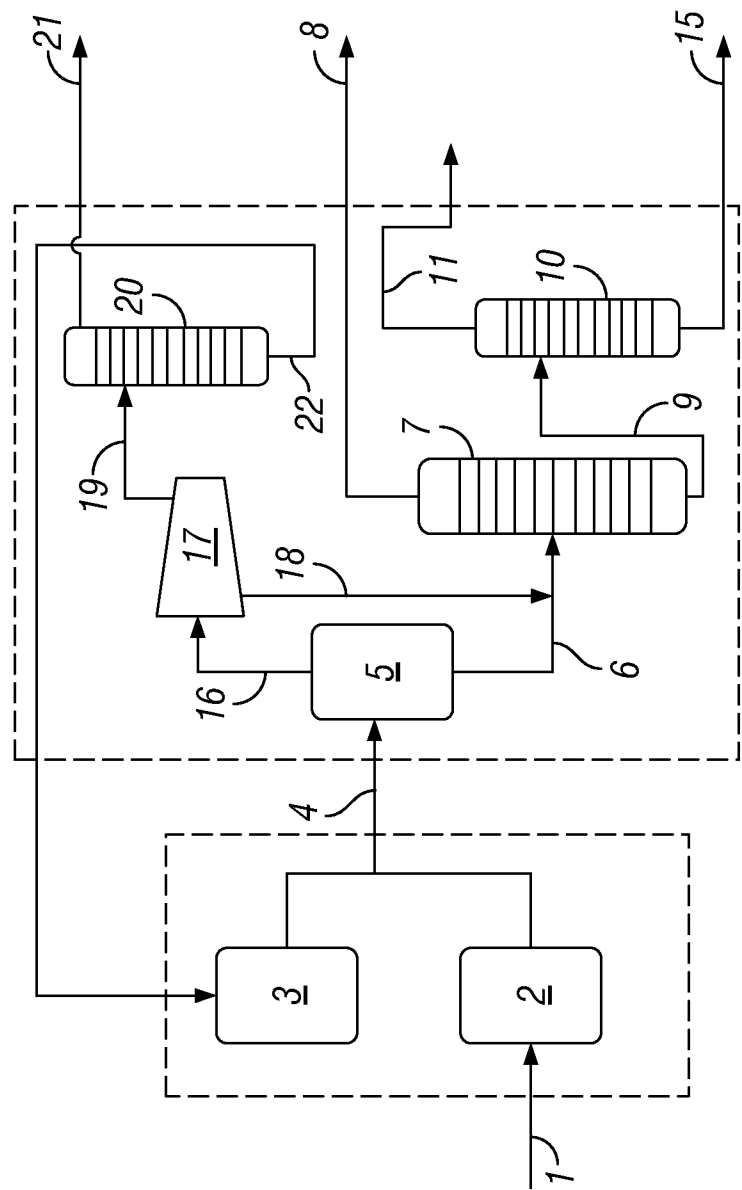


FIG. 3

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US 11/31917

A. CLASSIFICATION OF SUBJECT MATTER

IPC(8) - C07C 2/00 (2011.01)

USPC - 208/134; 585/486

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC(8): C07C 2/00 (2011.01); USPC: 208/134; 585/486

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched
USPC: 208/134; 585/486

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
Google Scholar, Google Patents, PubWEST (PGPB,USPT,EPAB,JPAB) (gasoline, blend, aromatic, hydrocarbon, benzene, toluene, xylene, naphthalene, separate, recover, collect, boil, catalyst, indane, indene, hydrodealkylate)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US 2009/0209794 A1 (Lauritzen, et al.) 20 Aug 2009 (20.08.2009) paragraphs [0023]-[0025], [0045]-[0046]	1-3, 4a
Y	US 2008/0051615 A1 (Stavens, et al.) 28 Feb 2008 (28.02.2008) paragraphs [0007], [0035]-[0040], [0048]-[0049], [0058], [0067]	1-3, 4a

☐ Further documents are listed in the continuation of Box C. ☐

* Special categories of cited documents:

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier application or patent but published on or after the international filing date

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

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

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

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

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

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

"&" document member of the same patent family

Date of the actual completion of the international search

27 Jul 2011 (27.07.2011)

Date of mailing of the international search report

12 AUG 2011

Name and mailing address of the ISA/US

Mail Stop PCT, Attn: ISA/US, Commissioner for Patents
P.O. Box 1450, Alexandria, Virginia 22313-1450

Facsimile No. 571-273-3201

Authorized officer:

Lee W. Young

PCT Helpdesk: 571-272-4300
PCT OSP: 571-272-7774

INTERNATIONAL SEARCH REPORT

International application No.

PCT/US 11/31917

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

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

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

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

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

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

This International Searching Authority found multiple inventions in this international application, as follows:
This application contains the following inventions or groups of inventions which are not so linked as to form a single general inventive concept under PCT Rule 13.1. In order for all inventions to be examined, the appropriate additional examination fees must be paid.

Group I: claims 1-3, 4a directed to an integrated process for producing gasoline blending components and aromatic hydrocarbons which comprises:

- (a) contacting a lower alkane feed with an aromatic hydrocarbon conversion catalyst to produce an aromatic reaction product mixture which is comprised of benzene and/or toluene and/or xylene, C9 aromatic products, C10 aromatic products including naphthalene and, optionally, C11+ aromatic products,
- (b) separating and recovering the aromatic reaction product mixture,
- (c) separating and recovering benzene, and
- (d) separating and recovering toluene and/or xylene and the C9 aromatic products and the C10 aromatic products which boil at a lower temperature than naphthalene from the naphthalene and the C10 aromatic reaction products which boil at a higher temperature than naphthalene and any C11 + aromatic products. —Continued on page 7—

1. ☐ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.
2. ☐ As all searchable claims could be searched without effort justifying additional fees, this Authority did not invite payment of additional fees.
3. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:
4. ☒ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:
1-3, 4a

Remark on Protest

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

INTERNATIONAL SEARCH REPORT
Information on patent family members

International application No.
PCT/US 11/31917

Continuation of Box No. III Observations where unity of invention is lacking

Group II: claims 5a, 4b, 5b directed to a gasoline blending component which comprises a component selected from the group consisting of indane, methyl indane, indene, methyl indene and mixtures thereof.

The inventions listed as Groups I-IV do not relate to a single general inventive concept under PCT Rule 13.1 because under PCT Rule 13.2 they lack the same or corresponding technical features for the following reasons:

Group I does not include the indane, methyl indane, indene and methyl indene of group II.

Group II does not include the catalytic reaction to produce aromatics with the subsequent separation of group I.

The common feature of gasoline blending components containing aromatics of group I and II is taught by US 3,493,492 A to Sze et al. (col 5, ln 29-31; col 5, ln 62 to col 6, ln 27); therefore the common feature is not an improvement over the prior art.

None of these technical features are common to the other groups, nor do they correspond to a special technical feature in the other groups. Therefore, unity of invention is lacking.

It is noted that there are two claims numbered 4 and 5, for the purpose of this opinion, the claims were renumbered to 4a, 4b, 5a, 5b.