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ABOGADOS ESPECIALISTAS

Señor
Jefe de la División de Nuevas Creaciones
Superintendencia de Industria y Comercio
E. S. D.

SUPERINTENDENCIA DE INDUSTRIA Y COMERCIO



No. 06-110780-00004-0000

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118 21 PATENTIS Eje 1: REGDLPPOSITO
Act: 538 PLICION Folios: 2

Expediente: **07-110780**

Referencia: Solicitud de la patente de invención denominada **"PROCESO PARA LA OBTENCIÓN DE HIDROCARBUROS LÍQUIDOS A PARTIR DE LA ROTURA DE MOLÉCULAS DE CARBONO E HIDRÓGENOS"**

Solicitante: **PEDRO A. SERVER BARCELO**

I. PETICIÓN

Yo, **JORGE E. VERA VARGAS**, obrando como apoderado de la parte solicitante, atentamente manifiesto a su Despacho que de conformidad con el artículo 44 de la Decisión 486 de la Comisión de la Comunidad Andina, comedidamente solicito a usted se sirva proceder a estudiar y examinar la patente de invención denominada: **"PROCESO PARA LA OBTENCIÓN DE HIDROCARBUROS LÍQUIDOS A PARTIR DE LA ROTURA DE MOLÉCULAS DE CARBONO E HIDRÓGENO"**, expediente No. 07-110780

II. PAGO DE TASAS.

Presento con este memorial el recibo de tasas oficiales por valor de **CUATROCIENTOS VEINTE MIL PESOS (\$420.000)**, correspondiente al examen de la patente de invención.

Bogotá, D.C., mayo de 2008

Señor Jefe,


JORGE E. VERA VARGAS
C.C. 17.150.455
T.P. 12.122

SUPERINTENDENCIA DE INDUSTRIA Y COMERCIO



No. 06-110780- -00004-0000

Fecha 2008-05-23 15:34:57 Dep. 2020 NULCRLACION
Hoja 2 PATENTES Lvs 1 REGISTRO
Act 538 PLICION Hoja 2

SUPERINTENDENCIA DE INDUSTRIA Y COMERCIO

NIT : 900176082-2

RECIBO OFICIAL DE CAJA : 08 - 40.966
: MAYO 21 DE 2008

***** CONSIGNACION *****

DEPOSITANTE	TIPO PAGO	BANCO	CUENTA	No. PAGO	FECHA PAGO	Vr. PAGO
VERA ABOGADOS ASOCIADOS	CONSIGNACION	BANCO DE BOGOTA	062754387	344612	21/05/2008	1,059,000.00

***** CONCEPTO *****

ANT. HISTORICO	CONCEPTO	TOTAL CONCEPTO
00/05-01-01. SOLICITUDES	85 EXAMEN DE PATENTABILIDAD DE INVEN	420,000.00
	TOTAL :	\$ 420,000.00

8541 CUATROCIENTOS VEINTE MIL PESOS

RESPONSABLE :

RECIBO DE CAJA APLICADO AL EXPEDIENTE No. _____

DIVISIÓN DE NUEVAS CREACIONES

RADICACIÓN EXPEDIENTE No. 06-110780

EL EXTRACTO DE LA PRESENTE SOLICITUD DE **PATENTE DE INVENCION**

FUE PUBLICADO EN LA GACETA DE PROPIEDAD INDUSTRIAL No **584** DE

FECHA **31 DE DICIEMBRE DE 2007** EL TÉRMINO HÁBIL SEÑALADO POR LA

LEY EXPIRA EL **31 DE MARZO DE 2008**

NOTA: Dentro del plazo de los seis (6) meses siguientes a partir de la fecha de publicación en la gaceta de Propiedad Industrial, deberá solicitar y cancelar el examen de patentabilidad so pena de que la solicitud caiga en abandono, de acuerdo con lo establecido en el Artículo 44 de la Decisión 486/2000.

SE PRESENTARON OPOSICIONES POR PARTE DE TERCEROS.

SI _____

NO X

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88



US005186722A

United States Patent [19]

[11] Patent Number: 5,186,722

Cantrell et al.

[45] Date of Patent: Feb. 16, 1993

[54] HYDROCARBON-BASED FUELS FROM BIOMASS

[75] Inventors: Charles L. Cantrell; Ngee S. Chong, both of Austin, Tex.

[73] Assignee: Cantrell Research, Incorporated, Austin, Tex.

[21] Appl. No.: 720,724

[22] Filed: Jun. 25, 1991

[51] Int. Cl.² C10M 1/04

[52] U.S. Cl. 44/605; 44/905; 585/14; 585/240; 585/242; 585/355; 585/356; 585/947

[58] Field of Search 585/240, 242, 355, 356, 585/947, 14; 44/605, 905

[56] References Cited

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Dialog Search Report Abstracts.

Primary Examiner—Jacqueline Howard
Attorney, Agent, or Firm—Arnold, White & Durkee

[57]

ABSTRACT

The invention relates to a process for providing fuels from biomass such as seed oils or plant fruits. Generally the process utilizes a metal catalyzed conversion to step to provide fuel mixtures with compositions that may be varied depending on conditions of temperature, pressure and time of reaction. Mixtures of hydrocarbons produced from limonene feedstocks include alicyclic, alkyl and aromatic species. Monocyclic aromatic compounds may be obtained in high yields depending on the reaction conditions employed.

29 Claims, 4 Drawing Sheets

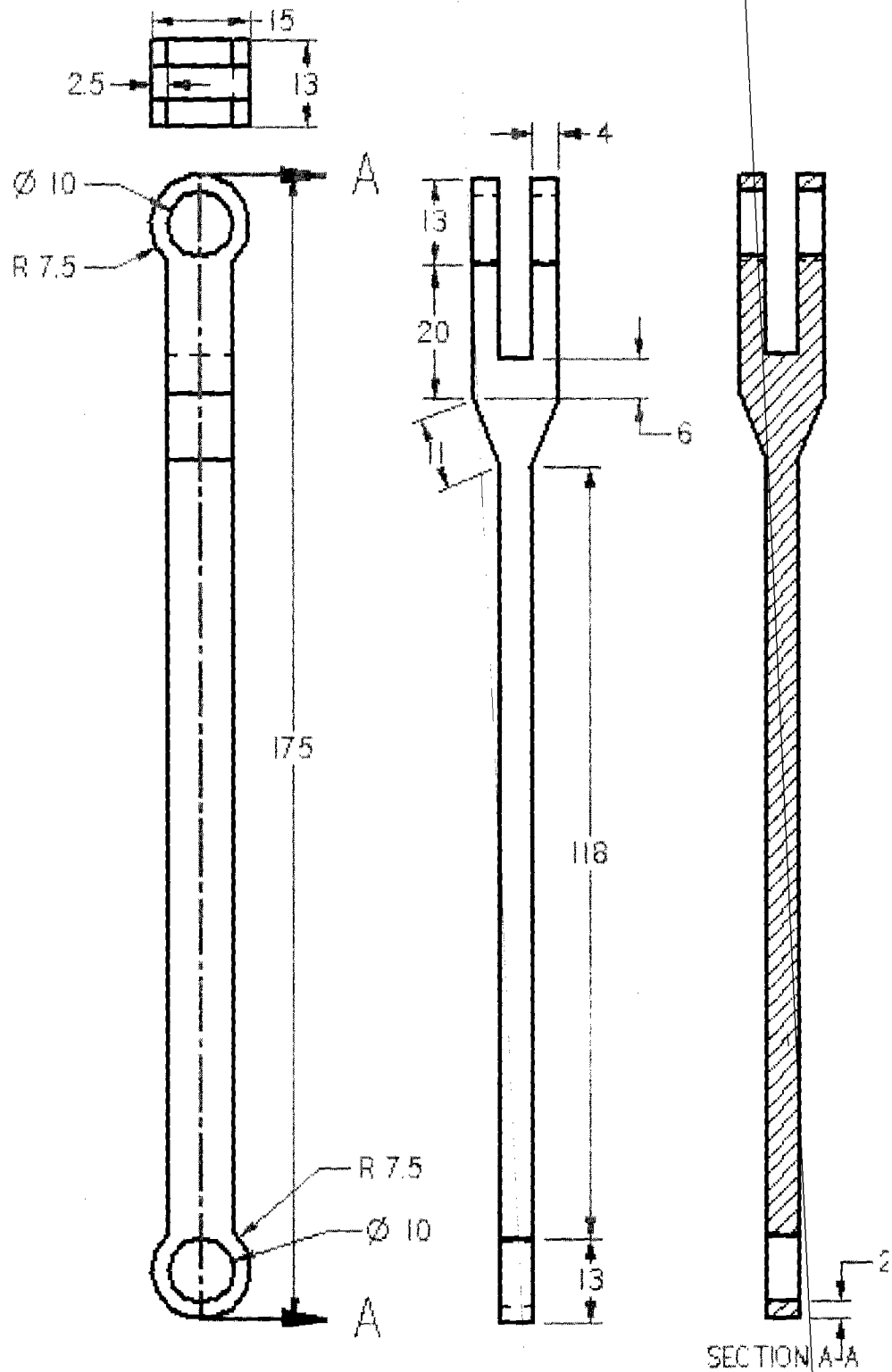


SOLID EDGE



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AL DISEÑAR CON EL COMPUTADOR

Planos para realizar las partes – EJE 2



HYDROCARBON-BASED FUELS FROM BIOMASS

BACKGROUND OF THE INVENTION

1. Field of the Invention

The invention relates generally to biomass fuels derived from plant sources. In particular aspects, the invention relates to a terpenoid-based fuel produced by a cracking/reduction process or by irradiation. The process may be controlled to produce a biomass fuel having variable percentages of benzenoid compounds useful, for example, as *per se* fuels, as fuel additives or as octane enhancers for conventional gasoline fuels.

2. Description of the Related Art

Increasing attention is being focused on problems associated with diminishing supplies of fossil fuels. These problems center on economic and ecologic considerations. It is recognized that oil and gas sources are exhaustible and that world politics may seriously jeopardize attempts to manage presently identified petroleum reserves. These are strong economic factors having potential effects on many facets of business and quality of life. There is also increasing concern over the pollution generated by fossil fuel burning which causes extensive and perhaps irreversible ecological harm. Consequently, fuel performance is becoming more of a concern, since highly efficient fuels, especially for internal combustion engines, will decrease or eliminate toxic emissions and cut operation costs.

Approaches to these problems have included efforts to develop total substitutes or compatible blends for petroleum-based fuels. For example, engines will operate efficiently on natural gas or alcohol. However, this requires engine modifications that are relatively expensive and at the present considered impractical in view of present production and sheer numbers of extant engines. With pure methanol, corrosion, particularly evident in upper-cylinder wear may be a problem (Schwartz, 1986).

Biomass sources have been explored as fuel source alternatives to petroleum. Biomass is defined as organic matter obtained from agriculture or agriculture products. Many side-products of foods, for example, are inefficiently used, leading to large amounts of organic waste. Use of such waste as a fuel *per se* or as a blend compatible with existing petroleum based fuels could extend limited petroleum reserves, reduce organic waste and, depending on the processing of the organic waste, provide a less expensive alternate fuel or fuel blends.

One of the more common components of plants and seeds is a group of alicyclic hydrocarbons classified as terpenes. Pinene and limonene are typical examples of monocyclic terpenes. Both have been tested as fuels or fuel additives. The Whitaker reference (1922) discloses the use of a terpene, as a blending agent for alcohol and gasoline or kerosene mixtures. A fuel containing up to about 15% of steam distilled pine oil was claimed to be useful as a motor fuel. Nevertheless, pinene was useful mainly to promote soluble mixtures of ethyl alcohol, kerosene and gasoline. There were no disclosed effects on fuel properties nor was there disclosed any further processing of the pinene.

Two United States patents describe a process for purifying limonene for use as a fuel or fuel additive (Whitworth, 1989, 1990). The process includes distillation of limonene-containing oil followed by removal of water. The distilled limonene, blended with an oxida-

tion inhibitor such as p-phenylenediamine, is claimed as a gasoline extender when added in amounts up to 20% volume. Unfortunately, in actual testing under a power load in a dynamometer, addition of 20% limonene to unleaded 87 octane gasoline results in serious preignition, casting serious questions as to its practical value as a gasoline extender.

On the other hand, Zundma (1946) discloses the use of alicyclic olefins such as limonene, cyclohexene, cyclopentene and menthene without modification as stabilization additives for gasoline. These compounds contain at least one double bond, a characteristic that apparently contributes to the antioxidant effect of adding these compounds to gasolines in amounts not exceeding 10% by volume.

U.S. Pat. No. 4,300,009 (Haag, 1981) is concerned with the conversion of biological materials to liquid fuels. Although relating in major part to zeolite catalytic conversion of plant hydrocarbons having weights over 150, a limonene/water feed was shown to produce about 19% toluene when pumped over a fixed bed zeolite catalyst at 482° C. at atmospheric pressure. Unfortunately, monocyclic aromatic compounds were reported to comprise only about 40% of the total products, of which major components were toluene and ethylbenzene. A disadvantage with the use of zeolite catalyst was the need to fractionate the aromatic compounds from the product mixture to obtain gasoline or products useful as chemicals. Formation of undesirable coke was also disclosed as a potential problem, in view of its tendency to inactivate zeolite catalysts.

Biomass fuel extenders such as methyltetrahydrofuran (MTHF) have been tested as alternative fuels (Rundolph and Thomas, 1988), but appear to be relatively expensive as pure fuels. As an additive in amounts up to about 10%, MTHF compares favorably with tetraethyl lead.

Fuel mixtures suitable as gasoline substitutes have also been prepared by mixing various components, for example C₂-C₇ hydrocarbons, C₄-C₁₂ hydrocarbons and toluene (Wilson, 1991). Toluene, and other substituted monocyclic benzenoid compounds such as 1,3,5-trimethylbenzene, 1,2,3,4-tetramethylbenzene, o-, m- and p-xylenes, are particularly desirable as octane enhancers in gasolines and may be used to supplement gasolines in fairly large percentages, at least up to 40 or 50 percent.

Generally, processes for obtaining aromatic compounds are synthetic procedures. Therefore it is relatively expensive to use aromatic liquid hydrocarbons as fuels or blends for gasoline fuels. On the other hand, a biomass source of easily isolated aromatic compounds would be less expensive, provide an efficient disposal of organic waste, and conserve petroleum reserves by extending or possibly replacing gasoline fuels. Although aromatic hydrocarbons occur naturally and are isolable from plant sources, it is impractical to isolate these compounds from biomass material because of the relatively low amounts present.

SUMMARY OF THE INVENTION

The present invention is intended to address one or more of the problems associated with dependence on fuels obtained from petroleum sources. The invention generally relates to a process of preparing hydrocarbon-based fuels from available plant components containing terpenoids. The process involves catalytic conversion

of one or more terpenoid compounds under conditions that may be varied to alter the product or products produced. Such products are generally mixtures of hydrocarbons useful as fuels *per se* or as fuel components.

The inventors have surprisingly discovered that biomass fuels may be appreciably improved through the application of catalytic conversion process techniques, heretofore utilized in cracking methods of processing petroleum crudes and related complex mixtures of petroleum fuels. Unexpectedly, it was also found that biomass fuels may under certain conditions be converted in exceptionally high yield to aromatic hydrocarbons comprising mixtures with significant octane boosting properties.

In one aspect, the invention involves a process for the preparation of a biomass fuel that includes conversion of a suitable feedstock by metal catalysts at an elevated temperature to a mixture of hydrocarbons, then obtaining the biomass fuel from the resulting hydrocarbon mixture. The isolated product or products will be derivatives or molecularly rearranged species of the feedstock material which itself may be obtained from a wide range of biomass sources.

Such a feedstock will typically include one or more terpenoid class compounds, preferably as a major component. This is commonly the case in many plants, especially in plant seeds or in parts of plants that have a high oil content, such as skins of citrus fruits or leaves. Numerous plant source oils are suitable including a variety of fruits, particularly citrus fruits, vegetables and agriculture products such as corn, wheat, eucalyptus, pine needles, lemon grass, peppermint, lavender, milkweed, tallow beans and other similar crops. Examples of terpenoid compounds found in leaves, seeds and other plant parts include α -pinenes, limonenes, menthols, linalools, terpinenes, camphenes and carenes, for example, which may be monounsaturated or more highly unsaturated. Preferred feedstock terpenoids are monocyclic. Limonenes are particularly preferable since they are found in high quantity in many plant oils. Limonene is useful in the optically inactive DL form or as the D or L isomer.

Feedstocks are generally more conveniently processed in liquid rather than solid form. Therefore, plant sources of terpenoids are usually extracted or crushed to obtain light or heavy oils. A particularly suitable oil is derived from citrus fruit, such as oranges, grapefruits or lemons. These oils are high in limonene content. Limonene feedstock oils, or for that matter any appropriate feedstock oil, need not be mixed with solvents and are conveniently directly catalytically converted and/or irradiated to provide hydrocarbon fuel mixtures.

In certain aspects, biomass-derived feedstocks are processed by metal catalyst conversion. Conversion is typically conducted at elevated temperatures in the range of 80° C. up to about 450° C., preferably between about 90° C. to 375° C. using limonene feedstock and most preferably in an inert atmosphere when high yields of monocyclic aromatic compounds are desired. When both a suitable catalyst and hydrogen are present, the catalytic conversion process leads to molecular rearrangements and hydrogenation, including intramolecular dehydrogenation ring cleavage and scission of carbon bonds.

Pressures may range from atmospheric to elevated pressures, e.g., up to 2,000 psi or above. The pressures employed determine the major products in the mixture

as well as the overall mixture composition of hydrocarbons obtained. In general it has been found that pressures from atmospheric up to about 500 psi result in production of monocyclic aromatic compounds as the major product. At higher pressures, aromatic species are usually not present and major products are fully reduced alicyclic products. In general it has been found that variations in temperature, pressure and time of reaction will affect product ratio and distribution. For example, when an inert gas is used to sparge the reaction mixture and pressures are close to atmospheric, 1-methyl-4-(1-methylethyl)benzene (p-cymene) is obtained in yields close to 85%.

Catalysts employed in the process are typically hydrogenation catalysts. These may include barium promoted copper chromate, Raney nickel, palladium, platinum, rhodium and the like. In a preferred embodiment, a noble metal catalyst such as 1%-5% palladium on activated carbon is effective. However, it will be appreciated that there are other types of catalysts that might be used in this process including mixed metal, metal-containing zeolites or organometallics. In some instances, it may be preferable to use alternate sources of hydrogen. Water or alcohols, for example, could be used as hydrogen sources.

After the catalytic conversion step, the catalyst is removed from the product mixture. In cases where a palladium or carbon catalyst is used, this is merely a matter of removing the catalyst by filtration or by decantation. Most catalysts may be regenerated or reused directly. As an optional step, an inert gas or hydrogen may be passed through the product mixture. This discourages product oxidation, especially when unsaturated compounds are present that are unusually susceptible to air oxidation. Furthermore, when high yields of monocyclic aromatic compounds are desired, as when limonene feedstock is employed, an inert gas bubbled or sparged through the reaction mixture improves yields. Nitrogen gas is preferred but other gases such as argon, xenon, helium, etc., could be used.

Reactions may be conducted on-line rather than in reactor vessels. Reaction rates and product formation would be adjusted by flow rates as well as parameters of pressure and temperature.

In usual practice, products obtained from the catalytic conversion process are distilled and may be collected over wide or narrow temperature ranges. Typically, a distillate is collected between 90° and 230° C. (as measured at atmospheric pressure). In a preferred embodiment, the distillate from a metal catalyzed conversion of limonene is collected between 90° and 180° C. The composition of this mixture will vary somewhat depending on the conditions under which the reaction is conducted; however, in general, the product mixture will include 2-3 major hydrocarbon components which may be mixed with conventional fuels such as gasoline or used without additional components as a fuel. Some of the components of the mixture, particularly aromatic species when present, may be further processed to isolate individual compounds.

Limonene is typically the major component of feedstocks from citrus oils. Under one set of selected conditions, that is, processing at 415° C., 1200 psi using a 5% palladium on carbon catalyst, the major components of the collected product are *cis* and *trans*, 1-methyl-4-(1-methylethyl) cyclohexane. Varying amounts of minor components may also be present, including hexane, 3,3,5-trimethylheptane, 1,1,5-dimethylhexyl-4-methyl-

5 cyclohexane, m-methane and 3,7,7-trimethylbicyclo-4,1,0-heptane. Minor components are typically less than 5%, and more usually, 1% or less.

Biomass fuel products produced by other variations of the process described may be obtained when lower pressures are used, that is, pressures less than 500 psi or under normal atmospheric conditions. In a run at 500 psi for example, the major products are cis and trans 1-methyl-4-(1-methylethylidene) cyclohexane and 1-methyl-4-(1-methylethyl) benzene. Minor components from this reaction typically include 1-methyl-4-(1-methylethyl) cyclohexene, limonene, hexane, 3,3-dimethylcyclohexane, 2,4-dimethyl-1-heptanol, dodecane, 3-methyl nonane and 3,4-dimethyl-1-decene. Minor products will tend to vary arising, for example, from contaminants in the feedstock or from air oxidation of primary products.

In a most preferred embodiment, limonene feedstock is heated to about 110° C. at atmospheric pressure under an inert atmosphere such as nitrogen. The inert gas is bubbled or sparged through the reaction mixture during the heating process. Under these conditions, the major product, often in excess of 84%, is 1-methyl-4-(1-methylethyl)benzene. Total minor products make up less than 1% of the product composition. The product, usually isolated by distillation, may be used directly as an octane-enhancer, as a fuel or in nonfuel applications, such as a solvent.

In another aspect of the invention, the biomass feedstock is irradiated and additionally subjected to catalytic conversion in the presence of hydrogen. The irradiation is preferably conducted with ultraviolet light in a wavelength range of 230 to 350 nanometers. In preferred practice, the irradiation is performed concurrently with catalytic conversion. The effect of the irradiation is to modify product distribution, most likely by the creation of free radicals which cause a variety of intramolecular rearrangements. Product distribution therefore may be different from the distribution obtained using only catalytic conversion. Generally used methods of irradiation include use of lamps with limited wavelength range in the ultraviolet or lamps with appropriate filters, for example 450 watt tungsten lamps with ultraviolet selective sleeves. The ultraviolet light may be directed toward a feedstock or aimed at the vapor of the reaction mixture under reflux conditions. Biomass fuel mixtures obtained from the combined irradiation/catalytic conversion typically produces mixtures in which the major components are cis and trans 1-methyl-4-(1-methylethyl) cyclohexane and 1-methyl-4-(1-methylethyl) benzene. Minor components in these mixtures are typically 3,3,5-trimethylheptane, 2,6,10,15-tetramethylheptadecane, 3-methylhexadecane, 3-methyl nonane and 3,4-dimethylcyclohexane ethanol. A preferred catalyst is palladium on activated carbon, however, other catalysts such as platinum, rhodium, iron, barium chromate and the like may be used.

In yet another aspect, the invention is directed to hydrocarbon mixtures such as obtained by the above described processes. Under selected conditions of reaction with a predominantly limonene feedstock, for example 500 psi, the product mixture will be chiefly hydrocarbons having formula typically $C_{10}H_{16}$, $C_{10}H_{18}$, and $C_{10}H_{20}$. Under the particular conditions used in a preferred embodiment, that is, temperature of 260° C., atmospheric pressure and a limonene feedstock, products typically include 1-methyl-4-(1-methylethyl) benzene, 1-methyl-4-(1-methylethylidene) cyclohexene,

and 1-methyl-4-(1-methylethyl) cyclohexane, and are typically obtained in a ratio of about 50:9:41. This mixture in combination with traditional gasoline fuels, for example, 87 octane gasoline, will boost octane when added in relatively low percentages. It may also be added to gasoline in amounts of 25% of total volume without detrimentally affecting engine performance. The $C_{10}H_{18}$ component of the mixture is a substituted cyclohexane and has been identified as having the formula 1-methyl-4-(1-methylethyl) cyclohexane, in cis and trans forms. The $C_{10}H_{16}$ major components are substituted benzene compounds typically having the structure 1-methyl-4-(1-methylethyl) benzene, although other substituted benzenes may be obtained depending on the conditions under which the process is conducted. The $C_{10}H_{20}$ component is typically a substituted cycloolefin, such as 1-methyl-4-(1-methylethylidene) cyclohexene.

In yet another aspect of the invention the biomass fuel produced by one or more of the foregoing processes may be used to increase octane and reduce emissions when blended with conventional gasolines and used in an internal combustion engine. The hydrocarbons or hydrocarbon mixture produced by the process combine with petroleum fuels, gasoline or diesel, for example, and may be used in amounts up to at least 25% by volume. Additionally, the hydrocarbon mixture or biomass product may be used alone to operate an internal combustion engine.

In still another aspect of the invention, an engine may be operated by supplying it with a hydrocarbon mixture produced by the process described. Purified limonene feedstocks, for example, when subjected to catalytic conversion at temperatures near 105° C. and ambient pressure produce products composed mainly of monocyclic aromatic compounds. By varying the reaction conditions, for example, increasing pressure or increasing the temperature, 1-methyl-4-(1-methylethyl) benzene is produced in yields of 30 to 84%. These various mixtures may be used directly or mixed in various amounts with gasoline, thus providing fuels which may be used to operate a combustion engine, for example an automobile engine.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1(a-f) shows the structures of some of the hydrocarbons produced by cracking/hydrogenation of limonene.

FIG. 2(a-b) shows the GC/MS of trans-1-methyl-4-(1-methylethyl) cyclohexane. Panel A is the mass spectrum of a standard sample. Panel B shows one of the compounds produced by the cracking/hydrogenation of limonene.

FIG. 3(a-b) shows the GC/MS of cis 1-methyl-4-(1-methylethyl) cyclohexane. Panel A is the mass spectrum of a standard sample. Panel B shows one of the compounds produced by the cracking/dehydrogenation of limonene.

FIG. 4(a-b) shows the GC/MS of 1-methyl-4-(1-methylethyl) benzene. Panel A is the mass spectrum of a standard sample. Panel B shows one of the major products produced by cracking/dehydrogenation of limonene under low pressure conditions.

DETAILED DESCRIPTION OF PREFERRED EMBODIMENTS

This invention concerns a novel process for producing various hydrocarbon fuels from biomass feedstocks,

typically plant extracts. Feedstocks are obtainable from a wide variety of plant sources such as citrus peels or seeds of most plant species. Oils are preferred as they have a high terpenoid content. Simple extraction meth-

While the list may appear extensive, it will be appreciated that biomass sources are ubiquitous and range from common agricultural products such as oranges to more exotic sources such as tropical plants.

TABLE I

BOTANICAL LIST		
Plant Oil: Containing of Terpenes or Terpene-derived Chemical Components (Useful as Fuel Additives)		
Plant Name	Botanical Species	Chemical Components
Angelica	<i>Angelica archangelica</i> L.	phellandrene, valeric acid
Anise	<i>Pimpinella anisum</i> L.	anethole, methylchavicol, anisaldehyde
Asarum	<i>Asarum canadense</i> L.	pinene, methyl Eugenol, borneol, linalyl acetate
Basil	<i>Malva officinalis</i> L.	citral
Bay or Myrica	<i>Cinnamomum</i> L.	methylchavicol, eucalyptol, linalool, eugenol, myrcene, chavicol, methylchavicol, methylchavicol, citral, phellandrene
Bergamot	<i>Citrus aurantium</i> L. (bergamia)	linalyl acetate, linalool, limonene, dipentene, bergapten
Bitter orange	<i>Citrus aurantium</i> L. (Rutaceae)	limonene, citral, decyl aldehyde, methyl anthranilate, anisole, terpinol
Capebot	<i>Melaleuca leucadendron</i> L.	eucalyptol (cinneol), pinene, terpinol, valeryl/terpene/aldehyde
Calamus	<i>Acorus calamus</i> L. (Aruaceae)	isovalone, calanone, calamot, camphene, pinene, asaronaldehyde
Camphor	<i>Cinnamomum camphora</i> L.	safrol, camphor, terpinol, eugenol, cineol, pinene, phellandrene, cadinene
Caraway	<i>Carum carvi</i> L. (Umbelliferae)	carvone, limonene
Cardamom	<i>Elettaria cardamomum</i> Marten	eucalyptol, sabinene, terpinol, borneol, limonene, terpinene, 1-terpinene, 4-terpinene
Cedar	<i>Thuja occidentalis</i> L.	pinene, thujone, fenchone
Celery	<i>Apium graveolens</i> L.	limonene, phendol, sedanolide, sedanol, methadiene
Chenopodium	<i>Chenopodium ambrosioides</i> L.	ascaridole, cymene, terpinene, limonene, methadiene
Cinnamon	<i>Cinnamomum cassia</i> Nees	cinnamaldehyde, cinnamyl acetate, eugenol
Citronella	<i>Cymbopogon nardus</i> L.	geraniol, citronellol, camphene, dipentene, linalool, bornyl acetate
Copala	<i>Copala haitian</i>	carvophyllene, cadinene
Coriander	<i>Coriandrum sativum</i> L.	linalool, linalyl acetate
Cubeb	<i>Piper cubeba</i> L.	dipentene, cadinene, cubeb camphor
Cumin	<i>Cuminum cyminum</i> L.	cuminaldehyde, cymene, pinene, dipentene
Cypress	<i>Cupressus sempervirens</i> L.	linalul, pinene, camphene, cymene, terpinol, cadinene, cypress camphor
Dill	<i>Anethum graveolens</i> L.	carvone, limonene, phellandrene
Dwarf pine needle	<i>Pinus moniana</i> Mill.	pinene, phellandrene, sylvanene, dipentene, cadinene, bornyl acetate
Eucalyptus	<i>Eucalyptus globulus</i>	pinene, phellandrene, terpinol, citronellol, geranyl acetate, eucadene, pulegone
Fennel	<i>Foeniculum vulgare</i> Mill.	anethole, fenchone, pinene, limonene, dipentene, phellandrene
Fig	<i>Ficus carica</i> L.	pinene, limonene, bornyl acetate
Flsphen	<i>Phlaphium edulis</i> L.	limonene, aldehydes
Geranium	<i>Geranium robertianum</i> L.	geraniol, citronellol, linalool
Ginger	<i>Zingiber officinale</i> Roscoe	Zingiberene, camphene, phellandrene, borneol, cineol, citral
Hops	<i>Humulus lupulus</i> L.	humulene, terpenes
Hyssop	<i>Hyssopus officinalis</i> L.	pinene, sesquiterpene
Juniper	<i>Juniperus communis</i> L.	pinene, cadinene, camphene, terpinol, juniper camphor
Lavender	<i>Lavandula officinalis</i> Chaix	linalyl esters, linalool, pinene, limonene, geranyl acetate
Lemon	<i>Citrus limonum</i> L.	limonene, terpinene, phellandrene, pinene, citral, citronellol, geranyl acetate
Lemon grass	<i>Cymbopogon citratus</i>	citral, methylheptenone, citronellol, geraniol, limonene, dipentene
Levamis	<i>Artemisia mercurialis</i>	eucalyptol
Marjoram	<i>Origanum onites</i>	linalool, geraniol, methylheptenone
Myrtle	<i>Myrica caroliniana</i> L.	terpenes, terpinene, terpinol
Niaouli	<i>Myrica caroliniana</i> L.	pinene, eucalyptol, dipentene, camphor
Nutmeg	<i>Myristica fragrans</i> Houtt.	cineol, terpinol, limonene, pinene
Orange	<i>Citrus aurantium</i>	camphene, pinene, dipentene, borneol, terpinol, geraniol, safrol, myristicin
Origanum	<i>Origanum onites</i> L.	limonene, citral, decyl aldehyde, methyl anthranilate, linalool, terpinol
Parsley	<i>Petroselinum hortense</i>	cineol, terpinene
Patchouli	<i>Pogostemon cubeb</i>	pinene, pinene
Peppermint	<i>Mentha piperita</i> L.	patchouliene, aldehyde, eugenol, sesquiterpene
Peppermint	<i>Mentha piperita</i> L.	pulegone, ketones, carbonyls, acids
Peppermint	<i>Mentha piperita</i> L.	menthyl, methyl esters, menthone, pinene, limonene, cadinene, phellandrene
Peppermint	<i>Mentha piperita</i> L.	linalyl acetate, geraniol, geranyl acetate, limonene
Peppermint	<i>Mentha piperita</i> L.	eugenol, sesquiterpene
Peppermint	<i>Mentha piperita</i> L.	dipentene, pinene, sylvanene, cadinene, bornyl acetate
Peppermint	<i>Mentha piperita</i> L.	borneol, bornyl esters, camphor, eucalyptol, pinene, camphene
Peppermint	<i>Mentha piperita</i> L.	citral
Peppermint	<i>Mentha piperita</i> L.	safrol, eugenol, pinene, phellandrene, sesquiterpene, camphor
Peppermint	<i>Mentha piperita</i> L.	safrol, sabinyl acetate, cadinene, pinene
Peppermint	<i>Mentha piperita</i> L.	eucalyptol, camphor, linalool, borneol, terpinol, camphene, sesquiterpene
Peppermint	<i>Mentha piperita</i> L.	eucalyptol, eugenol, methyl chavicol, pinene, monoterpene/terpene acids
Peppermint	<i>Mentha piperita</i> L.	thujone, borneol, camphor
Peppermint	<i>Mentha piperita</i> L.	thymol, carvacrol, cymene, pinene, linalool, bornyl acetate
Peppermint	<i>Mentha piperita</i> L.	bornyl esters, pinene, camphene, limonene
Peppermint	<i>Mentha piperita</i> L.	vetivone, vetivonal, vetivonic acid, vetivone, palmitic acid, hexanoic acid
Peppermint	<i>Mentha piperita</i> L.	thujone, fenchone, pinene
Peppermint	<i>Mentha piperita</i> L.	thujyl alcohol, thujyl acetate, thujone, phellandrene, cadinene
Peppermint	<i>Mentha piperita</i> L.	cineol

ods are suitable, including use of presses or distillations from pulp material. Table I provides an illustrative list of plant sources for terpenoids and related compounds, including species and description of specific parts.

The invention has been illustrated with purified limonene but purification of biomass feedstock should not be

critical in that the inventors have found that crude plant oil extracts, for example, may be used as feedstocks. The presence of other hydrocarbons and hydrocarbon derivatives may alter products and product ratios to some extent depending on the composition of feedstock and processing conditions, however, where alicyclic compounds are initially present as major components, the disclosed process is expected to provide hydrocarbon mixtures analogous to those obtained with limonene feedstocks.

The high yield of a substituted benzene from the catalytic conversion of limonene is an unexpected result. The disclosed process therefore offers a plant source for high yield of aromatic hydrocarbons and a method to convert plant hydrocarbons directly to fuel or fuel additive products.

The inventors have recognized that the carbonaceous compounds predominating in many biomass sources up until now have been of limited use as practical fuels, i.e., gasolines and the like, unless modified to render compatible with existing fuels. Ideally, fuel companies should improve fuel properties. The relatively simple disclosed process provides mixtures of hydrocarbon-type compounds that are gasoline fuel compatible and also improve fuel properties. The mixtures can be separated into individual components, e.g., by fractional distillation, or used in cuts as fuels per se or fuel additives.

The biomass fuel source may be any one or more of several sources. Preliminary treatment may involve crushing, pressing, squeezing or grinding the biomass to a sufficiently liquid state so that effective contact with a catalyst is possible. Orange peels, used as a source of limonene by the inventors, can be ground, then pressed with roller presses under relatively high pressure, e.g., up to 10,000 psi, to obtain an oil that is 60-70% limonene. As a practical matter, it is not necessary to purify or dry such a crude oil before processing. The inventors did in fact purify crude limonene from orange oil by a distillation process, but on a large scale and in economic terms, separation or removal of undesired components is more efficiently performed after obtaining a product mixture. The presence of small amounts of nonhydrocarbons, heterocyclic compounds and inorganic material generally has little effect on product performance or may be easily removed from the final product.

Feedstock, or in simple terms, the starting material, is catalytically converted to product. The process bears some similarity to cracking, although generally lower temperatures are used and no additives such as water need be included. Although "cracking" has long been used in the petroleum industry to "break up" heavy petroleum crudes such as sludges and heavy oils, the inventors have found that a similar process may be applied to simple plant-derived hydrocarbons to produce novel fuel components. Cracking as generally employed in the petroleum industry, involves heating heavy crudes at relatively high temperatures, often in the presence of a catalyst. Depending on the nature of the catalyst, the length of time of heating, temperature, pressure, etc., various molecular rearrangements occur, including breaking of bonds, isomerizations and cyclizations, leading frequently to lower molecular weight products.

While variations of cracking are routinely considered for processing of petroleum crudes, the inventors have discovered that when cracking methods are used on a single component, a mixture of reaction products is

obtained which unexpectedly enhance gasoline octane and/or act as a fuel extender. This is somewhat surprising since products resulting from heating limonene, for example, in the presence of a catalyst are not much different in molecular weight from the starting material. Thus when limonene is heated to about 370° C. in the presence of a metal catalyst the consequence is broken bonds, rearranged double bonds, and, when hydrogen is present, reduction of unsaturated compounds. At lower temperatures, e.g., 105° C., predominating products appear to arise from rearrangements rather than bond scission. At lower temperatures, an aromatic ring compound, a benzene derivative is commonly the main product from catalytic conversion of limonene. It is likely that this mononuclear aromatic species results from some mechanism that isomerizes the external double bond of limonene into the ring, then dehydrogenates to fully aromatize the ring. In any event, the reaction process has been shown to give efficient production of 1-methyl-4-(1-methylethyl) benzene from limonene with yields exceeding 84% achieved in a single step process.

There are many ways one could run the reaction that converts limonene, or other like compounds or mixtures, to compounds that make useful fuels or fuel additives. The process is essentially a single-step operation. As one example, one simply places limonene in a suitable vessel, adds a catalyst such as platinum or palladium on carbon, then heats the oil to about 90°-180° C. An inert gas or, alternatively, hydrogen may be passed through the mixture. The reaction is monitored over some period of time, e.g., about two hours for reactions on the scale of about 2 liters and depending on the amount of catalyst, size of vessel, etc. Monitoring by gas chromatography, for example, is by withdrawing some liquid from the reaction vessel and injecting directly onto the column of a gas chromatograph. When desirable compounds have formed, the reaction may be terminated. This is done by removing the hydrogen source if hydrogen is used, cooling the oil, filtering off the catalyst, if necessary, and then purifying any product desired.

Products are generally isolated by distillation which is rapid and simple. It may be done from the same process vessel as the catalytic conversion, thus utilizing a batch process. If this route is taken, catalyst should be removed as it might explode or catch fire if hydrogen gas is adsorbed on its surface, as is the case with platinum on carbon. But catalysts that are readily removed may be used, for example, an immobilized catalyst which is lifted from the reaction vessel. In any event, the product is generally a liquid which may be fractionally distilled into single or mixtures of products based on relative boiling points.

The following is a description of the analytical methods used including the dynamometer and test engine set up for determining fuel properties.

Chromatography

Gas chromatography was conducted using a Hewlett-Packard 5890 Series II gas chromatograph equipped with a Hewlett-Packard Vectra 386/25 for data acquisition. Gas chromatography/mass spectrometry was performed using a Hewlett-Packard 5971A MSD with a DB wax 0.25 mm i.d. 1 μ capillary column.

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Dynamometer

The dynamometer used for testing was purchased from Super Flo (Colorado Springs, Colo.), model SF 901 with a full computer package which included a Hewlett-Packard model Vectra ES computer. Standard heat exchangers were added. Data were recorded using a HP model 7475A X-Y plotter.

Test Engine

The test engine was constructed from high nickel alloy Bowtie blocks (General Motors, Detroit, Mich.) with stainless steel billet main caps, block machined to parallel and square to the main bearing bore with dimensions set and honed with a torque plate. Tolerances were 0.0001 inch on the cylinder diameters and tapers. Pistons, purchased from J & E (Cordova, Calif.) were machined to a wall tolerance of 0.003 inch. Pistons and connecting rod pins were fit to a tolerance of 0.0013 inch. The pistons were lined up in the deck blocks (9" in depth) at zero deck. Bottom assembly was blueprinted to tolerances of 0.0001 inch.

The engine was an 8-cylinder Pontiac with raised port cylinder heads. These were ported, polished and flowed by Racing Induction Systems (Conover, N.C.) for even fuel distribution. Camshafts were tested for 1850-7200 rpm at 106° intake centerline to 108° intake center line.

The examples which follow are intended to illustrate the practice of the present invention and are not intended to be limiting. Although the invention is demonstrated with highly purified limonene feedstocks, the starting material used in the disclosed process is not necessarily limited to a single compound, or even to terpenoid compounds. A wide range of hydrocarbon feedstocks could be used, including waste hydrocarbons from industrial processes. One value of the process lies in the potential to utilize biomass sources, often considered waste products, in providing fuels from sources independent of petroleum interests.

Many variations in experimental conditions are possible, leading to numerous product combinations. Differences in temperature and pressure (compare Examples 1, 2, 4 and 5) will determine the type and yield of products obtained.

EXAMPLE 1

Catalytic Conversion of Limonene to Aromatic Rich Product (Method A)

600 ml of purified d-limonene was placed in a 1-liter flask with 12.5 g of 1% Pd on carbon. The mixture was heated to 105° C. for 2 hr at ambient pressure while bubbling nitrogen through the solution. After cooling to room temperature, the catalyst was removed by filtration. The clear, colorless liquid was distilled at atmospheric pressure and the fraction boiling between 175°-178° C. collected as a clear colorless liquid which had a specific gravity of 0.85 g/ml. Gas chromatographic analysis of the collected product showed two peaks. Mass spectrometry of the product components and comparison with published libraries of known compounds were used to identify 1-methyl-4-(1-methylethyl)benzene and 1-methyl-4-(1-methylethyl)cyclohexene as the products. Structures are shown in FIG. 1. Mass spectra are shown in FIG. 2. Table 1, showing relative amounts of the mixture components, indicates product composition is over 80% 1-methyl-4-(1-methylethyl)benzene and 17% 1-methyl-4-(1-methylethyl)cyclohexene.

thylcyclohexene. Minor amounts of 1-methyl-4-(1-methylethyl)cyclohexane and trace amounts, less than 1%, of other hydrocarbon components were also detected.

TABLE 1

Composition of Products Formed in the Catalytic Reactions of d-Limonene

Chemical Name	Formula	Product (%)
1-MMEC ¹	C ₁₁ H ₂₀	2
c-MMEC ²	C ₁₁ H ₂₀	17
1-methyl-4-(1-methylethyl)cyclohexene	C ₁₁ H ₁₈	81
1-methyl-4-(1-methylethyl)cyclohexane	C ₁₁ H ₂₀	Trace
1-MMEC = trans-1-methyl-4-(1-methylethyl)cyclohexene		
c-MMEC = cis-1-methyl-4-(1-methylethyl)cyclohexene		

EXAMPLE 2

Catalytic Conversion of Limonene to Saturated Hydrocarbon Products (Method B)

2.0 liters of purified limonene was placed in a 4.2 liter stainless steel cylinder with 40 g of 5% Pd on carbon. Initial pressure was 1200 psi with heating at 365°-370° C. for five hours. Pressure increased to 1750 psi during heating and fell to 500 after the cylinder was cooled to room temperature. Specific gravity of the product mixture was 0.788 g/ml. Mass spectrometric/gas chromatographic analysis showed two major products: 1-methyl-4-(1-methylethyl)cyclohexane (cis and trans isomers). Trace amounts (<0.01%) included hexane, 3,3,3-trimethyl heptane, 1-(1,5-dimethylhexyl)-4-methylcyclohexane, 1S,3R-(+)- and 1S,3S-(+)-m-menthane and cyclohexanepropionic acid.

Product composition is shown in Table 2.

TABLE 2

Composition of Products Formed in the Catalytic Reactions of d-Limonene

Chemical Name	Formula	Product (%)
3,3,3-trimethyl heptane	C ₁₀ H ₂₂	Trace
DMHMC ¹	C ₁₁ H ₂₀	Trace
c-MMEC ²	C ₁₁ H ₂₀	69.58
1-methyl-4-(1-methylethyl)cyclohexane	C ₁₁ H ₂₀	30.34
Cyclohexanepropionic acid	C ₁₁ H ₂₀	Trace
1S,3S-(+)-m-menthane	C ₁₀ H ₂₀	Trace
1S,3R-(+)-m-menthane	C ₁₀ H ₂₀	Trace

¹DMHMC = 1-(1,5-dimethylhexyl)-4-methylcyclohexane
²c-MMEC = cis-1-methyl-4-(1-methylethyl)cyclohexane

EXAMPLE 3

Engine Tests on 87 Octane Gasoline Blended with Limonene

Gasoline obtained locally from retail gasoline stations was tested on a dynamometer constructed and set up as described for the test engine. Exxon 87 octane gasoline was used as a control. Test samples were prepared by adding 5%, 10% or 20% limonene to Shamrock 87 octane gasoline. All samples were run under the same test conditions. Results of these tests are shown in Tables 3-6.

Table 3 shows the results of dynamometer tests with Exxon 87 octane gasoline. Engine knock sufficient to cause automatic shutdown of the test dynamometer described in Example 1, occurred above 3250 rpm.

Tables 4-6 show the effect of adding increasing amounts of limonene to Shamrock 87 octane gasoline. As shown in Table 4, engine shutdown occurred above

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3000 rpm with the addition of 5% limonene and above 2250 rpm with 10% limonene. In the presence of 20% limonene, serious preignition occurred shortly after starting at 2000 rpm, causing automatic shutdown of the test engine. Preignition was severe, causing explosive

Cylinder temperature, indicated from thermocouple measurements on each cylinder, showed a tendency to decrease when the biomass fuel mixture was added to gasoline. This indicated a decrease in heat of combustion.

TABLE 3

Standard Corrected Data for 29.92 inches Hg, 60 F, dry air, Test #113														
Test: 250 RPM Step Test	Fuel Spec. Grav.	740	Air Sensor	6.5										
Vapor Pressure: 35	Barometric Pres.	29.62	Ratio	1.00 to 1										
Engine Type: 4-Cycle Spark	Engine Displacement	358.0	Stroke	1.480										
Speed (rpm)	CBTQ (in./hr)	CRPQ (in./hr)	FHP (hp)	VE %	ME %	FA (A)	A/F (lb/lb)	BSFC (lb/hr)	CAT (in./hr)	Oil (in./hr)	Wat (in./hr)	BSAC (lb/hr)		
2000	126.3	124.3	11.4	66.7	87.2	52.5	166.3	14.5	.44	77	190	0	6.43	
2250	140.0	145.7	20.3	67.1	87.7	61.6	192.7	14.4	.44	77	194	0	6.35	
2500	158.5	161.3	24.3	86.6	86.4	66.8	212.5	14.6	.41	77	196	0	6.37	
2750	183.2	179.3	28.1	87.5	86.0	72.1	236.2	15.0	.42	77	197	0	6.34	
3000	160.8	186.5	32.1	88.2	85.6	80.3	250.5	14.6	.42	77	199	0	6.23	
3250	152.6	218.3	36.4	89.0	85.2	88.4	283.8	14.7	.42	77	200	0	6.24	
3500	167.7	26.5	41.3	14.4	36.8	11.7	48.3	20.0	.41	77	206	0	9.47	

SF-901 Dynamometer Test Data

Test: 250 RPM Step Test	Fuel Spec. Grav.	740	Air Sensor	6.5				
Vapor Pressure: 35	Barometric Pres.	29.62	Ratio	1.00 to 1				
Engine Type: 4-Cycle Spark	Engine Displacement	358.0	Stroke	1.480				
Thermocouple Temperature								
1	2	3	4	5	6	7	8	
1300	1290	1160	1220	1210	110	1180	1220	
1510	1275	1162	1220	1210	110	1210	1250	
1700	1270	1170	1225	1229	160	1230	1280	
1890	1270	1180	1240	1230	130	1240	1300	
2080	1270	1200	1270	1250	460	1270	1310	
2260	1270	1270	1290	1270	600	1290	1320	
2450	1260	1180	1240	1230	350	1240	1270	
2630	1190	1130	1150	1180	320	1190	1220	
2820	1140	1080	1090	1130	400	1140	1190	

TABLE 4

Standard Corrected Data for 29.92 inches Hg, 60 F, dry air, Test #114														
Test: 250 RPM Step Test	Fuel Spec. Grav.	747	Air Sensor	6.5										
Vapor Pressure: 35	Barometric Pres.	29.62	Ratio	1.00 to 1										
Engine Type: 4-Cycle Spark	Engine Displacement	358.0	Stroke	1.480										
Speed (rpm)	CBTQ (in./hr)	CRPQ (in./hr)	FHP (hp)	VE %	ME %	FA (A)	A/F (lb/lb)	BSFC (lb/hr)	CAT (in./hr)	Oil (in./hr)	Wat (in./hr)	BSAC (lb/hr)		
2000	126.3	124.3	11.4	66.7	87.2	52.5	166.3	14.5	.44	77	190	0	6.43	
2250	140.0	145.7	20.3	67.1	87.7	61.6	192.7	14.4	.44	77	194	0	6.35	
2500	158.5	161.3	24.3	86.6	86.4	66.8	212.5	14.6	.41	77	196	0	6.37	
2750	183.2	179.3	28.1	87.5	86.0	72.1	236.2	15.0	.42	77	197	0	6.34	
3000	160.8	186.5	32.1	88.2	85.6	80.3	250.5	14.6	.42	77	199	0	6.23	
3250	152.6	218.3	36.4	89.0	85.2	88.4	283.8	14.7	.42	77	200	0	6.24	
3500	167.7	26.5	41.3	14.4	36.8	11.7	48.3	20.0	.41	77	206	0	9.47	

SF-901 Dynamometer Test Data

Test: 250 RPM Step Test	Fuel Spec. Grav.	747	Air Sensor	6.5					
Vapor Pressure: 35	Barometric Pres.	29.62	Ratio	1.00 to 1					
Engine Type: 4-Cycle Spark	Engine Displacement	358.0	Stroke	1.480					
Thermocouple Temperature									
1	2	3	4	5	6	7	8		
1120	1130	980	990	1010	420	1110	1090		
1370	1130	1040	1050	1090	240	1150	1140		
1590	1150	1070	1090	1090	170	1190	1190		
1780	1180	1110	1150	1140	140	1240	1230		
1970	1220	1150	1200	1180	110	1240	1250		
2160	1190	1100	1130	1120	110	1180	1200		
2350	1140	1030	1020	1050	200	1100	1120		
2540	1060	1040	990	990	1010	1040	1050		

knocking just prior to shutdown

TABLE 5

Standard Corrected Data for 29.92 inches Hg, 60 F, dry air, Test #115														
Test: 250 RPM Step Test	Fuel Spec. Grav.	753	Air Sensor	6.5										
Vapor Pressure: 35	Barometric Pres.	29.61	Ratio	1.00 to 1										
Engine Type: 4-Cycle Spark	Engine Displacement	358.0	Stroke	1.480										
Speed (rpm)	CBTQ (in./hr)	CRPQ (in./hr)	FHP (hp)	VE %	ME %	FA (A)	A/F (lb/lb)	BSFC (lb/hr)	CAT (in./hr)	Oil (in./hr)	Wat (in./hr)	BSAC (lb/hr)		
2000	124.9	124.9	17.4	86.5	87.3	54.4	169.6	14.3	.46	77	191	0	6.52	
2250	147.5	146.5	20.7	87.0	87.1	61.8	191.9	14.1	.44	77	193	0	6.29	

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TABLE 5-continued

2500	166	175	24.3	17.3	39.6	8.9	42.6	22.0	.46	77	195	0	6.29	
2750	2.1	1.1	26.1	8.4	.0	8.5	27.7	12.5	.00	77	196	0	.4	
3000	2.2	1.3	32.1	2.7	.0	0	11.0	0	.00	77	197	0	.9	
3250	2.3	1.4	36.4	2.3	.0	2.3	7.4	14.8	.00	77	198	0	.9	

SF-901 Dynamometer Test Data

Test: 250 RPM Step Test	Fuel Spec. Grav.	753	Air Sensor	6.5				
Vapor Pressure: 35	Barometric Pres.	29.61	Ratio	1.00 to 1				
Engine Type: 4-Cycle Spark	Engine Displacement:	358.0	Stroke:	3.480				
<u>Thermocouple Temperature</u>								
1	2	3	4	5	6	7	8	
1300	1270	1140	1200	1210	130	1220	1240	
1500	1260	1160	1210	1210	120	1230	1260	
1700	1230	1110	1150	1160	130	1190	1210	
1900	1180	1070	1090	1110	110	1140	1160	
2100	1100	1020	1050	1060	100	1060	1090	
2300	1040	970	1000	1010	130	990	1020	

TABLE 6

Standard Corrected Data for 29.92 inches Hg, 60 F, dry air													Test #116	
Test: 150 RPM Step Test	Fuel Spec. Grav.	768	Air Sensor	6.5										
Vapor Pressure: 35	Barometric Pres.	29.62	Ratio	1.00 to 1										
Engine Type: 4-Cycle Spark	Engine Displacement	358.0	Stroke	1.480										
Speed (rpm)	CBTQ (in./hr)	CRPQ (in./hr)	FHP (hp)	VE %	ME %	FA (A)	A/F (lb/lb)	BSFC (lb/hr)	CAT (in./hr)	Oil (in./hr)	Wat (in./hr)	BSAC (lb/hr)		
2000	131.7	126.3	17.4	84.7	87.4	52.6	166.2	14.5	.44	77	190	0	6.43	
2250	157.0	159.9	20.7	17.5	45.1	9.0	38.6	19.7	.62	77	194	0	12.25	
2500	2.0	1.0	24.5	6.1	0	0	14.9	0	.00	77	194	0	.01	
2750	2.4	1.1	28.1	1.4	0	0	9.1	0	.00	77	194	0	.01	
3000	2.2	1.3	32.1	2.2	0	0	9.9	0	.00	77	196	0	.01	

mixture distilled. The distillate was collected over a range of 110°-180° C.

Mixture components were 45% $C_{10}H_{14}$ and about 55% $C_{10}H_{16}$ with trace amounts of 1-methyl-4-(1-methylethyl)-cyclohexene, cis-p-menth-8(10)-en-ol, 3-methyl nonane and 1-methyl-3-(1-methylethyl) benzene as determined by gas chromatography.

EXAMPLE 6

Engine Tests on 87 Octane Gasoline Blended With Biomass Fuel or MTBE

A biomass fuel mixture was prepared under substantially the same conditions of Example 1. The mixture was added in 10% and 20% by volume to Mobil 87 octane gasoline purchased from local retail gasoline stations. Another mixture was prepared by adding methyl tert-butyl ether (MTBE) to 87 octane Mobil gasoline in 10% by volume. Dyno test were run on all mixtures using the aforementioned test engine. Table 9 shows results of dynamometer tests on Mobil 87 octane gasoline; Table 10 shows results of addition of 10% by volume biomass fuel mixture and Table 11 results of addition of 20% of biomass fuel to the 87 octane gasoline. Not shown are results with the MTBE blend which were similar to results obtained with the blend containing 10% biomass fuel mixture.

Results showed that addition of up to 20% of the biomass generated fuel mixture caused no decrease in horsepower or torque at rpms in the range up to about

fuel mixture in about 10% by volume to the 87 octane gasoline provided about 1% increase in horsepower and torque at 4250 rpms (compare Table, third column, and Table 10, third column). Addition of 20% by volume of the biomass fuel mixture did not significantly change horsepower or torque up to about 4250 rpms when compared with 87 octane gasoline (compare Table 9, third column, and Table 11, third column). MTBE added at 10% by volume was similar in effect to the blend containing 10% biomass fuel mixture in averaging increases in horsepower of about 0.7-1.1%.

Additionally, as the amount of biomass fuel mixture added to conventional gasoline was increased, the A/F (air-to-fuel ratio) ratio decreased somewhat. Cylinder temperature, measured in each cylinder by thermocouple, did not appear to be significantly affected.

TABLE 8

Composition of Products Formed in the Catalytic Conversion of Limonene

Chemical Name	Formula	Product (%)
1-MMTCT	$C_{10}H_{16}$	37.6
2-MMTCT	$C_{10}H_{16}$	16.7
cis-p-menth-8(10)-en-ol	$C_{10}H_{18}O$	<1
1-methyl-4-(1-methylethyl)-cyclohexene	$C_{10}H_{18}$	<1
1-methyl-3-(1-methylethyl)benzene	$C_{11}H_{14}$	45.1
3-methyl nonane	$C_{10}H_{22}$	<1

1-MMTCT = 1-methyl-4-(1-methylethyl)-cyclohexene

2-MMTCT = 2-methyl-4-(1-methylethyl)-cyclohexene

TABLE 9

Standard Corrected Data for 29.92 inches Hg, 60° F, dry air, Test #134

Test: 250 RPM Step Test	Fuel Spec: Grav	732 Air Sensor	6.5
Vapor Pressure: 91	Barometric Pres	29.33 Ratio	1.00 to 1
Engine Type: 4-Cycle Spark	Engine displacement	355.0 Stroke	3.480
Speed: CB/Tq CB/Pwr FHP	VE % ME % B/Btr scfm A/F	BSFC	BSAC
rpm lb-ft Hp	Hp	lb/Hr CAT Oil Wai	lb/Hp-hr
2000 333.4 121.7 17.3 77.8 87.2 58.4 147.3 11.6 46 77 199 170 5.71			
2250 339.8 145.2 20.6 79.1 86.7 67.1 168.9 11.6 46 77 199 167 5.74			
2500 345.5 164.3 24.1 79.1 86.5 101.6 186.7 8.4 67 77 200 170 5.65			
2750 350.7 183.6 27.9 79.7 85.9 112.9 206.9 8.4 67 77 200 170 5.60			
3000 362.4 207.0 31.8 81.0 85.7 113.8 229.3 9.3 60 77 201 169 5.5			
3250 369.4 228.6 36.1 81.7 85.4 124.5 250.7 9.2 58 77 205 169 5.45			
3500 375.8 250.4 40.7 82.7 85.0 135.2 273.7 9.1 56 77 202 169 5.41			
3750 378.3 270.8 46.0 83.7 84.5 141.2 296.1 9.6 55 77 203 169 5.44			
4000 377.2 287.3 51.6 84.3 83.7 148.6 317.5 9.9 55 77 203 169 5.50			
4250 379.1 306.8 57.5 85.1 83.1 159.2 341.5 9.9 56 77 204 170 5.54			

SF-901 Dynamometer Test Data

Test: 250 RPM Step Test				Fuel Spec: Grav		732 Air Sensor		6.5	
Vapor Pressure: 91				Barometric Pres		29.33 Ratio		1.00 to 1	
Engine Type: 4 Cycle Spark				Engine Displacement		355.0 Stroke		3.480	
Thermocouple Temperature									
1		2		3		4		5	
1250	1260	1270	1280	1290	1300	1310	1320	1330	1340
1240	1250	1180	1190	1100	1110	1120	1130	1090	1080
1250	1260	1200	1140	1100	1110	1120	1130	1090	1080
1270	1280	1230	1180	1120	1130	1140	1150	1100	1090
1280	1290	1250	1160	1140	1140	1140	1140	1110	1100
1290	1300	1270	1220	1160	1160	1160	1160	1130	1120
1300	1310	1280	1210	1170	1160	1160	1160	1130	1120
1320	1330	1300	1230	1180	1170	1170	1170	1140	1130
1330	1340	1310	1240	1190	1180	1180	1180	1150	1140
1350	1360	1330	1260	1200	1190	1190	1190	1160	1150
1360	1370	1350	1270	1210	1200	1200	1200	1170	1160
1370	1380	1360	1280	1220	1210	1210	1210	1180	1170
1380	1390	1370	1290	1230	1220	1220	1220	1190	1180
1390	1400	1380	1300	1240	1230	1230	1230	1200	1190
1400	1410	1390	1310	1250	1240	1240	1240	1210	1200
1410	1420	1400	1320	1260	1250	1250	1250	1220	1210
1420	1430	1410	1330	1270	1260	1260	1260	1230	1220
1430	1440	1420	1340	1280	1270	1270	1270	1240	1230
1440	1450	1430	1350	1290	1280	1280	1280	1250	1240
1450	1460	1440	1360	1300	1290	1290	1290	1260	1250
1460	1470	1450	1370	1310	1300	1300	1300	1270	1260
1470	1480	1460	1380	1320	1310	1310	1310	1280	1270
1480	1490	1470	1390	1330	1320	1320	1320	1290	1280
1490	1500	1480	1400	1340	1330	1330	1330	1300	1290
1500	1510	1490	1410	1350	1340	1340	1340	1310	1300
1510	1520	1500	1420	1360	1350	1350	1350	1320	1310
1520	1530	1510	1430	1370	1360	1360	1360	1330	1320
1530	1540	1520	1440	1380	1370	1370	1370	1340	1330
1540	1550	1530	1450	1390	1380	1380	1380	1350	1340
1550	1560	1540	1460	1400	1390	1390	1390	1360	1350
1560	1570	1550	1470	1410	1400	1400	1400	1370	1360
1570	1580	1560	1480	1420	1410	1410	1410	1380	1370
1580	1590	1570	1490	1430	1420	1420	1420	1390	1380
1590	1600	1580	1500	1440	1430	1430	1430	1400	1390
1600	1610	1590	1510	1450	1440	1440	1440	1410	1400
1610	1620	1600	1520	1460	1450	1450	1450	1420	1410
1620	1630	1610	1530	1470	1460	1460	1460	1430	1420
1630	1640	1620	1540	1480	1470	1470	1470	1440	1430
1640	1650	1630	1550	1490	1480	1480	1480	1450	1440
1650	1660	1640	1560	1500	1490	1490	1490	1460	1450
1660	1670	1650	1570	1510	1500	1500	1500	1470	1460
1670	1680	1660	1580	1520	1510	1510	1510	1480	1470
1680	1690	1670	1590	1530	1520	1520	1520	1490	1480
1690	1700	1680	1600	1540	1530	1530	1530	1500	1490
1700	1710	1690	1610	1550	1540	1540	1540	1510	1500
1710	1720	1700	1620	1560	1550	1550	1550	1520	1510
1720	1730	1710	1630	1570	1560	1560	1560	1530	1520
1730	1740	1720	1640	1580	1570	1570	1570	1540	1530
1740	1750	1730	1650	1590	1580	1580	1580	1550	1540
1750	1760	1740	1660	1600	1590	1590	1590	1560	1550
1760	1770	1750	1670	1610	1600	1600	1600	1570	1560
1770	1780	1760	1680	1620	1610	1610	1610	1580	1570
1780	1790	1770	1690	1630	1620	1620	1620	1590	1580
1790	1800	1780	1700	1640	1630	1630	1630	1600	1590
1800	1810	1790	1710	1650	1640	1640	1640	1610	1600
1810	1820	1800	1720	1660	1650	1650	1650	1620	1610
1820	1830	1810	1730	1670	1660	1660	1660	1630	1620
1830	1840	1820	1740	1680	1670	1670	1670	1640	1630
1840	1850	1830	1750	1690	1680	1680	1680	1650	1640
1850	1860	1840	1760	1700	1690	1690	1690	1660	1650
1860	1870	1850	1770	1710	1700	1700	1700	1670	1660
1870	1880	1860	1780	1720	1710	1710	1710	1680	1670
1880	1890	1870	1790	1730	1720	1720	1720	1690	1680
1890	1900	1880	1800	1740	1730	1730	1730	1700	1690
1900	1910	1890	1810	1750	1740	1740	1740	1710	1700
1910	1920	1900	1820	1760	1750	1750	1750	1720	1710
1920	1930	1910	1830	1770	1760	1760	1760	1730	1720
1930	1940	1920	1840	1780	1770	1770	1770	1740	1730
1940	1950	1930	1850	1790	1780	1780	1780	1750	1740
1950	1960	1940	1860	1800	1790	1790	1790	1760	1750
1960	1970	1950	1870	1810	1800	1800	1800	1770	1760
1970	1980	1960	1880	1820	1810	1810	1810	1780	1770
1980	1990	1970	1890	1830	1820	1820	1820	1790	1780
1990	2000	1980	1900	1840	1830	1830	1830	1800	1790
2000	2010	1990	1910	1850	1840	1840	1840	1810	1800
2010	2020	2000	1920	1860	1850	1850	1850	1820	1810
2020	2030	2010	1930	1870	1860	1860	1860	1830	1820
2030	2040	2020	1940	1880	1870	1870	1870	1840	1830
2040	2050	2030	1950	1890	1880	1880	1880	1850	1840
2050	2060	2040	1960	1900	1890	1890	1890	1860	1850
2060	2070	2050	1970	1910	1900	1900	1900	1870	1860
2070	2080	2060	1980	1920	1910	1910	1910	1880	1870
2080	2090	2070	1990	1930	1920	1920	1920	1890	1880
2090	2100	2080	2000	1940	1930	1930	1930	1900	1890
2100	2110	2090	2010	1950	1940	1940	1940	1910	1900
2110	2120	2100	2020	1960	1950	1950	1950	1920	1910
2120	2130	2110	2030	1970	1960	1960	1960	1930	1920
2130	2140	2120	2040	1980	1970	1970	1970	1940	1930
2140	2150	2130	2050	1990	1980	1980	1980	1950	1940
2150	2160	2140	2060	2000	1990	1990	1990	1960	1950
2160	2170	2150	2070	2010	2000	2000	2000	1970	1960
2170	2180	2160	2080	2020	2010	2010	2010	1980	1970
2180	2190	2170	2090	2030	2020	2020	2020	1990	1980
2190	2200	2180	2100	2040	2030	2030	2030	2000	1990
2200	2210	2190	2110	2050	2040	2040	2040	2010	2000
2210	2220	2200	2120	2060	2050	2050	2050	2020	2010
2220	2230	2210	2130	2070	2060	2060	2060	2030	2020
2230	2240	2220	2140	2080	2070	2070	2070	2040	2030
2240	2250	2230	2150	2090	2080	2080	2080	2050	2040
2250	2260	2240	2160	2100	2090	2090	2090	2060	2050
2260	2270	2250	2170	2110	2100	2100	2100	2070	2060
2270	2280	2260	2180	2120	2110	2110	2110	2080	2070
2280	2290	2270	2190	2130	2120	2120	2120	2090	2080
2290	2300	2280	2200	2140	2130	2130	2130	2100	2090
2300	2310	2290	2210	2150	2140	2140	2140	2110	2100
2310	2320	2300	2220	2160	2150	2150	2150	2120	2110
2320	2330	2310	2230	2170	2160	2160	2160	2130	2120
2330	2340	2320	2240	2180	2170	2170	2170	2140	2130
2340	2350	2330	2250	2190	2180	2180	2180	2150	2140
2350	2360	2340	2260	2200	2190	2190	2190	2160	2150
2360	2370	2350	2270	2210	2200	2200	2200	2170	2160
2370	2380	2360	2280	2220	2210	2210	2210	2180	2170
2380	2390	2370	2290	2230	2220	2220	2220	2190	2180
2390	2400	2380	2300	2240	2230	2230	2230	2200	2190
2400	2410	2390	2310	2250	2240	2240	2240	2210	2200
2410	2420	2400	2320	2260	2250	2250	2250	2220	2210
2420	2430	2410	2330	2270	2260	2260	2260	2230	2220
2430	2440	2420	2340	2280	2270	2270	2270	2240	2230
2440	2450	2430	2350	2290	2280	2280	2280	2250	2240
2450	2460	2440	2360	2300	2290	2290	2290	2260	2250
2460	2470	2450	2370	2310	2300	2300	2300	2270	2260
2470	2480	2460	2380	2320	2310	2310	2310	2280	2270
2480	2490	2470	2390	2330	2320	2320	2320	2290	2280
2490	2500	2480	2400	2340	2330	2330	2330	2300	2290
2500	2510	2490	2410	2350	2340	2340	2340	2310	2300
2510	2520	2500	2420	2360	2350	2350	2350	2320	2310
2520	2530	2510	2430	2370	2360	2360	2360	2330	2320
2530	2540	2520	2440	2380	2370	2370	2370	2340	2330
2540	2550	2530	2450	2390	2380	2380	2380	2350	2340

TABLE 12 continued

Engine Type: 4-Cycle Spark	Engine Displacement: 155.0 Stroke: 1.440			
Speed: CBTq	HP	FA	AI	BSFC
rpm	lb-ft	in	in	lb/Hp-hr
2000	326.0	124.1	17.3	78.2
2250	336.8	144.3	20.6	79.1
2500	344.5	164.0	24.1	79.0
2750	349.1	182.8	27.9	78.9
3000	360.9	206.2	31.8	80.2
3250	367.8	227.6	36.1	81.0
3500	374.1	249.1	40.7	82.9
3750	375.8	268.3	46.0	82.9
4000	372.3	283.5	51.6	82.8
4250	371.9	300.9	57.5	83.5

SI 90.1 Dynamometer Test Data									
Test: 250 RPM Step Test	Fuel Spec: CBTq	AI Sensor: 6.5							
Vapor Pressure: 91	Barometric: 29.47	Ratio: 1.0161							
Engine Type: 4-Cycle Spark	Engine Displacement: 155.0	Stroke: 1.440							
Thermocouple Temperature									
1	2	3	4	5	6	7	8		
1250	1290	1180	1240	1110	1280	1240	1330		
1320	1310	1190	1260	1060	1300	1250	1370		
1400	1340	1210	1280	1010	1320	1260	1380		
1500	1370	1230	1340	1070	1340	1285	1380		
1600	1370	1240	1360	1110	1360	1280	1400		
1700	1350	1240	1380	1150	1380	1270	1410		
1800	1340	1280	1260	1160	1400	1280	1420		
1900	1370	1250	1290	1170	1420	1310	1430		
2000	1390	1260	1310	1210	1450	1340	1420		
2100	1370	1380	1300	1340	1470	1310	1490		

SI 90.1 Dynapometer Test Data

Test: 250 RPM Step Test
 Vapor Pressure: 91
 Engine Type: 4 Cycle Spark

Fuel Spec: 155.0

Barometer: 29.42

Engine Displacement: 155.0

Stroke: 1.440

Thermocouple Temperature

1	2	3	4	5	6	7	8
1250	1290	1280	1290	1310	1280	1290	1330
1250	1310	1300	1300	1300	1300	1250	1370
1280	1320	1310	1300	1300	1320	1260	1380
1270	1320	1260	1270	1280	1340	1250	1380
1270	1330	1260	1260	1270	1360	1260	1400
1250	1350	1280	1270	1270	1380	1270	1410
1340	1360	1280	1260	1260	1400	1290	1420
1270	1370	1290	1290	1310	1420	1310	1450
1250	1390	1280	1320	1320	1450	1300	1470
1370	1380	1300	1340	1370	1470	1310	1490

The present invention has been described in terms of particular embodiments found by the inventors to comprise preferred modes of practice of the invention. It will be appreciated by those of skill in the art that in light of the present disclosure modifications and changes can be made in the particular embodiments exemplified without departing from the intended scope of the invention. For example, numerous modifications of reaction conditions could be employed to vary product composition, including use of non-traditional catalysts, combinations of low temperatures and high pressures, oxygen or hydrogen donors added to the feedstock and the like. All such modifications are intended to be included within the scope of the claims.

REFERENCES

- The references cited within the text are incorporated by reference to the extent they supplement, explain, provide background for or teach methodology, techniques and/or compositions employed herein.
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- Rudolph, T. W. and Thomas, J. J., Biomass 16, 33 (1988).
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- Whitworth, R. D., U.S. Pat. No. 4,818,250, Apr. 4, 1989.
- Whitworth, R. D., U.S. Pat. No. 4,915,707, Apr. 10, 1990.
- Wilson, E. J. A., U.S. Pat. No. 5,006,850, Apr. 2, (1991).
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We claim:

1. A process for the preparation of a biomass fuel having an octane number of at least 95, comprising the steps:

obtaining a feedstock that includes one or more terpenoids;
 converting the feedstock in a liquid phase at a temperature between about 80° C. to about 150° C. at ambient pressure in the presence of a matrix-supported single metal catalyst selected from a group consisting essentially of platinum, palladium or rhodium for a period of time sufficient to produce a hydrocarbon fuel mixture having at least 70% monocyclic aromatic hydrocarbon content wherein said hydrocarbon mixture contains up to 3% of volatile hydrocarbons with vapor pressures of at least 0.17 psi at 100° C. and contains less than 2% of aliphatic olefins and polycyclic aromatic hydrocarbon components.

2. The process of claim 1 wherein the biomass feedstock is obtained from citrus fruits or oils, seeds of plants, or leaves of plants.

3. The process of claim 1 wherein the terpeneoid comprises a monocyclic terpene.

4. The process of claim 3 wherein the monocyclic terpene comprises d-limonene, d-limonene or l-limonene.

5. The process of claim 1 wherein the biomass feedstock is converted at a temperature between 90°-210° C.

6. The process of claim 2 wherein the biomass feedstock is obtained from the fruits, seeds or leaves by solvent extraction or mechanical pressing.

7. The process of claim 1 wherein the biomass feedstock, said feedstock comprising limonene, is converted at 90°-120° C. over a palladium catalyst to provide a hydrocarbon mixture comprising at least 80% monocyclic aromatic compounds.

8. The process of claim 7 further comprising reacting in an inert atmosphere.

9. The process of claim 7 wherein the palladium catalyst is 1% palladium on carbon added at about 10 g/600 ml of limonene feedstock.

10. The process of claim 7 wherein the hydrocarbon mixture comprises 1-methyl-4-(1-methylethyl)benzene and 1-methyl-4-(1-methylethyl)cyclohexane.

11. The process of claim 10 wherein the hydrocarbon mixture further comprises cis- and trans-1-methyl-4-(1-methylethyl)cyclohexane.

12. The process of claim 1 further comprising irradiating the feedstock with ultraviolet light.

13. The process of claim 12 wherein the feedstock is simultaneously irradiated and catalytically converted.

14. The process of claim 13 wherein the feedstock is irradiated at a wavelength within the range of 230-350 nm.

15. The process of claim 13 wherein the feedstock is irradiated in a hydrogen atmosphere.

16. The process of claim 13 wherein the feedstock is irradiated in the presence of 5% Pd on activated carbon.

17. The process of claim 7 wherein the limonene feedstock is irradiated in the presence of hydrogen and a catalyst for a period of time sufficient to produce a hydrocarbon mixture, said mixture comprising major components cis- and trans-1-methyl-4-(1-methylethyl)cyclohexane, 1-methyl-4-(1-methylethylidene)cyclohexane and 1-methyl-1-(4-methylethyl)benzene.

18. The process of claim 17, wherein said hydrocarbon mixture further comprises 3,3,5-trimethylheptane, 2,6,10,15-tetramethylheptadecane, 3-methylhexadecane, 3-methyl nonane and 3,4-dimethyl cyclohexane ethanol.

19. A process for converting biomass to a hydrocarbon fuel, comprising the steps:

obtaining the biomass from a plant oil, seed, leaves or fruit wherein the biomass is provided from chemical or mechanical extraction; and

converting the biomass in a liquid phase to the hydrocarbon fuel at 365°-370° C. in the presence of a palladium or platinum metal on carbon catalyst at a pressure of between 800 psi and 2000 psi for a time sufficient to form a hydrocarbon fuel mixture consisting essentially of cis- and trans-1-methyl-4-(1-methylethyl)cyclohexane and up to 3% of low molecular weight saturated hydrocarbons with vapor pressures greater than about 0.17 psi at 100° C. wherein the hydrocarbon fuel mixture is substantially free of olefins and aromatic hydrocarbons.

20. The process of claim 19 wherein the hydrocarbon mixture comprises cis- and trans-1-methyl-4-(1-methylethyl) cyclohexane.

21. The process of claim 20 wherein the hydrocarbon mixture further comprises 3,3,5-trimethyl heptane, 1(1,5-dimethylhexyl)-4-methyl cyclohexane, 1S,3R-(+)-(H)-menthane, 1S,1S-(H)-menthane and cyclohexanepropionic acid.

22. A hydrocarbon composition capable of boosting octane in gasoline fuels for internal combustion engines, comprising hydrocarbons having formulae $C_{10}H_{14}$, $C_{10}H_{16}$, and $C_{10}H_{18}$ with a ratio of about 80:17:3 wherein the $C_{10}H_{14}$ is 1-methyl-4-(1-methylethyl)benzene, $C_{10}H_{16}$ is 1-methyl-4-(1-methylethyl)cyclohexane and $C_{10}H_{18}$ is a mixture of cis- and trans-1-methyl-4-(1-methyl)cyclohexane.

23. A method of increasing octane and reducing emissions in an internal combustion engine comprising blending a biomass fuel produced by the process of claim 1 with a fossil fuel.

24. The method of claim 23 wherein the biomass fuel comprises up to 100% (v/v) of the fossil fuel.

25. The method of claim 24 wherein the fossil fuel is gasoline.

26. A method of running a fossil-fuel engine without modification of said engine, comprising the steps:

obtaining a biomass feedstock that includes one or more terpenes;

converting the feedstock to a hydrocarbon mixture according to claim 1; and

supplying said hydrocarbon mixture to an engine in an amount sufficient to run said engine.

27. The method of claim 26 wherein the monocyclic aromatic compound is 1-methyl-4-(1-methylethyl)benzene.

28. A biomass fuel produced by the method of claim 1 or claim 17.

29. A hydrocarbon composition biomass fuel having an octane rating of at least 95 consisting essentially of 1-methyl-4-(1-methylethyl)benzene, menthene and aliphatic or alicyclic hydrocarbons from a group consisting essentially of 3,3,5-trimethylheptane, 4-methyl-1,3-pentadiene and 1-methyl-4-(1-methylethyl)cyclohexane wherein the aliphatic hydrocarbons are present at about 1-3% by volume and the 1-methyl-4-(1-methylethyl)benzene is at least about 70% by volume.

94

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95
98

**SUPERINTENDENCIA DE INDUSTRIA Y COMERCIO
DIRECCION DE NUEVAS CREACIONES**

2020

Abogado
JORGE E. VERA VARGAS

ASUNTO	Radicación	06-110780
	Trámite	002
	Evento	001
	Actuación	430
	Oficio	16
	Folios	07

Patente de Invención ☒ Patente de Modelo de Utilidad ☐

Vía Nacional ☒

Como resultado del examen de fondo, realizado con fundamento en el artículo 45 de la Decisión 486 de la Comisión de la Comunidad Andina, se le comunica:

1. Documentos estudiados

Descripción:	Folios: 4 a 17	como se radico inicialmente
Reivindicaciones:	Folios: 18 a 21	como se radico inicialmente
Figuras:	Folios: 23	como se radico inicialmente

2. Objeto de la invención

Título de la invención

Proceso para la obtención de hidrocarburos líquidos a partir de la rotura de moléculas de carbono e hidrógenos (folio 1).

El problema planteado en esta solicitud consiste en obtener gasoil u otro hidrocarburo a partir de materias primas naturales, como biomasa y desechos de cualquier tipo.

Para solucionar este problema técnico se desarrolla un proceso a partir de la ruptura de moléculas de carbono e hidrogeno a través energía cinética y de rozamiento con reactivos.

Clasificación Internacional de Patentes (IPC) C10G47/18, C10G31/00.

3. De la solicitud de Patente (según el caso)

Descripción (artículo 28 D 486)

La descripción no divulga la invención de manera suficientemente clara y completa para su comprensión y para que una persona capacitada en la materia técnica correspondiente pueda ejecutarla, ya que no incluye la siguiente información:

- Una descripción de la invención en términos que permitan la comprensión del problema técnico y de la solución aportada por la invención.
- Una reseña de los dibujos, cuando los hubiera. Dado que no son claras las figuras. Las figuras deben enumerar todos los elementos constitutivos, de tal

Exp 2006 110780

forma que dicha numeración no se repita, sin ningún tipo de cotas, lectura explicativa o escalas y cada figura debe estar descrita completamente en el capítulo descriptivo.

- Se debe mejorar la calidad visual de los dibujos, ya que los actuales no permiten la comprensión de la solicitud. Ver anexo 1. ejemplos de redacción de las reivindicaciones para una solicitud de patente.
- Una descripción de la mejor manera conocida por el solicitante para ejecutar o llevar a la práctica la invención, utilizando ejemplos y referencias a los dibujos, de ser pertinentes.
- La información de las características técnicas de la invención no son suficientes para que un técnico experto en la materia pueda realizarla, ya que no se presentan las etapas y condiciones de estas que inciden sobre la materia para obtener un producto o un resultado.

Por lo anterior, la descripción no cumple con el requisito de claridad y/o divulgación completa lo que haría difícil su comprensión y ejecución de acuerdo al art. 28 de de la Decisión 486.

Como puede observarse la descripción tiene serios problemas de claridad y suficiencia pero se le indica al solicitante que respecto a la información requerida, no se admitirá modificaciones que amplíen el objeto inicial de la invención, sin perjuicio de lo anterior se aceptaran: (i) documentos relevantes del estado de la técnica no citados siempre y cuando no incluya aclaraciones, o comentarios del solicitante, respecto a la invención; (ii) adaptación de la descripción a las reivindicaciones; (iii) otras de naturaleza similar.

Reivindicaciones (artículo 30 D 486)

- La reivindicación independiente 1 no es clara en definir la materia a proteger. Al respecto no debe olvidarse lo dicho por el Tribunal Andino de Justicia respecto a las reivindicaciones de procedimiento (proceso):
"El objeto de la invención de procedimiento se encuentra conformado por "una serie o sucesión de operaciones que inciden sobre una materia (sólida, líquida o gaseosa) que se encamina a la obtención de una cosa o un resultado". (Otero Lastres, José Manuel. Ob. Cit)¹.
- De hecho la reivindicación 1 menciona que el proceso esta conformado por diferentes etapas, pero no las define y no detalla las condiciones técnicas de cada una de estas, que evidencien una ventaja o un efecto inesperado de la invención.
- Los términos "primera parte físico/mecánica", "segunda parte: química" y "cualquier otro residuo", en la reivindicación 1 y 2, utilizados para definir varias características del proceso, deben eliminarse. Estos términos no permiten definir las características técnicas de la invención, no siendo estas precisas y por lo tanto no claras, ya que no permiten una comparación con el estado de la técnica.
- La reivindicación 2 describe las materias primas que pueden ser utilizadas en el proceso, pero la frase "y cualquier otro residuo", hace que la solicitud sea más amplia que el justificado en la extensión de la descripción, ya que esta incluye un número infinito de materiales que por su estructura química y física, no pueden comportarse de la misma forma al aplicarse el proceso reivindicado.
- La reivindicación 3 no es clara en definir las condiciones para la trituración, cizallamiento y rozamiento de la materia prima y cuales son los elementos exotérmicos que elevan la temperatura. Además, no define a que temperatura ocurre la ruptura de nivel molecular para cada posible materia prima utilizada.

¹Proceso 129-IP-2007

- La reivindicación 4 no es clara en definir el tipo de reacción que ocurre para obtener los hidrocarburos líquidos, es decir, no se definen los reactivos, los productos ni las condiciones a las cuales ocurren estas.
- La reivindicación 5 no define el límite al que se eleva la temperatura y las condiciones de secado de cada materia utilizada en el proceso.
- La reivindicación 6 no define la viscosidad a la que se homogeniza la materia prima y la temperatura a la que se logra esta para cada posible materia prima.
- La reivindicación 7 no tiene soporte en la descripción. Dado que en el capítulo descriptivo nunca se menciona que era necesario un análisis, reconocimiento y cuantificación de las sustancias químicas activas. Así mismo, no se divulga que tipo de análisis es el necesario y como se efectúa para cada una de las diversas materias primas mencionadas.
- Las reivindicaciones 10, 11, 14 y 15 incluyen como características técnicas el resultado a alcanzar de acuerdo con ciertas condiciones físico/mecánicas y químicas, lo cual es inaceptable. No se aceptan reivindicaciones que caractericen resultados, usos, contenidos, ventajas o efectos. Por lo anterior, las reivindicaciones citadas deben eliminarse del capítulo en cuestión.

En conclusión, el capítulo reivindicatorio no cumple con el requisito de claridad y soporte en la descripción de acuerdo con el artículo 30 de la Decisión 486.

4. Determinación del Estado de la Técnica

La fecha para determinar el estado de la técnica es el 10 de octubre de 2006 de acuerdo a la fecha prioridad reivindicada.

Teniendo en cuenta la anterior fecha indicada, se realiza la búsqueda de las anterioridades de la presente solicitud, encontrándose los siguientes documentos relevantes:

Nº	Documento	Título	Fecha de publicación
D1	US5186722	HYDROCARBON-BASED FUELS FROM BIOMASS	1993-02-16

5. Análisis de patentabilidad (según requisito) (artículo 14 D486)

Es importante mencionar que el siguiente análisis de patentabilidad se realizó teniendo en cuenta las objeciones del numeral 3 de la presente comunicación.

Novedad (artículo 16 D486)

Respecto a la reivindicación 1

La reivindicación independiente 1 menciona: "Proceso para la obtención de hidrocarburos líquidos a partir de la rotura de moléculas de carbono e hidrógeno caracterizado por estar conformado principalmente por diferentes etapas: en una primera parte físico/mecánica y diferentes etapas en una segunda parte: química".

Respecto al estado de la técnica:

D1 describe un proceso para preparar aceites hidrocarburos a partir de componentes vegetales que tienen terpenoides. El proceso incluye una conversión catalítica de uno o más terpenoides bajo condiciones que pueden ser cambiadas dependiendo del producto o productos a ser obtenidos.

Respecto a la solicitud en estudio:

D1 describe un proceso para producir varios aceites hidrocarburos a partir de biomasa como materias primas (Col 6 líneas 67-68). La fuente de aceites de biomasa puede ser de una o más fuentes. Un tratamiento preliminar consisten en moler, presionar, etc .para obtener el mayor líquido posible y hacer más eficiente el contacto con el catalizador. La materia prima es catalíticamente convertida en producto. El proceso ocurre de manera similar que un craqueo. Produciendo un rompimiento de los enlaces, isomerización y ciclaciones, logrando productos con un bajo peso molecular (Col líneas 29-64). Finalmente los productos son aislados por destilación (Col 10 línea 45).

De acuerdo a lo descrito en la anterioridad D1 se observa que todas las características técnicas de la reivindicación 1 ya eran conocidas en el estado de la técnica ya que muestra proceso para la obtención de hidrocarburos líquidos a partir de la ruptura de moléculas de carbono e hidrógeno que utiliza como materias primas la biomasa.

Dado lo anterior, el objeto de la invención recogido en la reivindicación 1 ha sido divulgado idénticamente en la anterioridad D1 por lo tanto esta reivindicación y sus dependientes no se pueden considerarse nuevas.

6. Conclusión:

Los requisitos de patentabilidad de la presente solicitud se encuentran afectados así:

N°	Documento	Reivindicaciones afectadas	Requisito que afecta
D1	US5186722	1-15	Novedad

En cumplimiento del artículo 45 de la Decisión 486 de la Comisión de la Comunidad Andina, se le indica que debe dar respuesta dentro del término de 60 días contados a partir de la fecha de notificación de la presente comunicación. En caso de no dar respuesta al presente requerimiento, o si a pesar de la respuesta subsistieran los impedimentos para la concesión, se denegará la patente.

Notifíquese el presente oficio conforme a lo dispuesto en el numeral 5.2, literal e), del capítulo quinto del título primero de la Circular Única N° 10 de 2001.

ALIX CARMENZA CÉSPEDES DE VERGEL
Directora de Nuevas Creaciones (C)

El anterior requerimiento fue notificado por fijación en lista, de fecha 04 NOV 2010

CONCEPTO TÉCNICO No. 3725	EXAMINADOR TÉCNICO Código No. 202090
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ANEXO 1

Explicación detallada de los Dibujos:

Las figuras o dibujos deben permitir una mejor comprensión del problema planteado y su solución, por lo tanto, las figuras y dibujos deben ser descritos en forma completa para que cumplan su función.

Si se incluyen dibujos se deben describir inicialmente en forma breve dentro de la descripción tal como: "Figura 1 muestra una vista lateral de la maquina empacadora; Figura 2 vista parcial de la máquina de la Figura 1"; y a continuación realizar una descripción detallada haciendo referencia a los dibujos, el nombre del elemento debe estar seguido del numero de referencia por ejemplo "la máquina de empaquetar 10 comprende dos rodillos accionados por un motor 11 para soportar y hacer girar el rollo 13".

La descripción y los dibujos deben ser consistentes los unos con los otros al referirse a los signos, símbolos o números de referencia.

En este apartado figuran las leyendas o explicaciones adicionales que requieren los dibujos que van a formar parte de la patente. Se trata de una explicación detallada, ya que no se permite la inclusión de ningún texto en las figuras, solo se admiten palabras dentro de las figuras que sean esenciales para la comprensión de los dibujos, como por ejemplo, "vapor", "agua", "abierto", "corte según AB o similares.

Ver Ejemplo de redacción de la descripción para una solicitud de patente.

Dibujos:

Los dibujos, planos, figuras y representaciones gráficas tienen como finalidad contribuir a una mejor comprensión y divulgación de la invención. Los dibujos deben estar explicados en la descripción. Tienen que ser esquemáticos, libre de detalles inútiles, de leyendas y palabras, poniendo en evidencia lo esencial, o sea, las características de la invención, por lo tanto deberán tener ciertas características:

- deben tener relación directa con la descripción;
- deben permitir visualizar las formas de ejecución descritas;
- la relación entre la descripción y los dibujos se debe hacer por medio de signos de referencia que se encuentren en ambos elementos y guarden una correspondencia;
- si dentro de la descripción han sido mencionados algunas figuras, necesariamente deben estar incluidas;
- no deben considerarse figuras o dibujos que no hayan sido descritos;
- deben ser enumerados individualmente y consecutivamente.

Ejemplo de redacción de la descripción para una solicitud de patente:

Sacacorchos.

Comenzar con el título de la invención

Objeto de la invención

sector tecnológico al que se refiere o al que se aplica la invención

La presente invención se refiere a un sacacorchos, concretamente a un sacacorchos que ha sido especialmente concebido para la apertura de botellas provistas de un tapón de madera, tapón para el que, por su propia naturaleza, son inoperantes los sacacorchos convencionales utilizados con los clásicos tapones de corcho.

Estado de la técnica

Todo lo que el solicitante conoce sobre los antecedentes de la invención

El propio solicitante es titular del modelo de utilidad con número de solicitud U 200300291, consistente en un tapón de madera, destinado a mantener el cierre estanco de un recipiente preferentemente tipo botella, como los utilizados en el envasado de vinos u otros productos, en sustitución del clásico tapón de corcho.

De forma más concreta el citado tapón de madera, cuenta con una cabeza exterior, destinada a quedar fuera de la botella, y con un cuerpo afectado por un orificio axial ciego y por una pluralidad de profundas acanaladuras perimetrales que facilitan la absorción de ligeras deformaciones producidas por el efecto del crecimiento de la madera al humedecerse.

El perfecto ajuste inicial entre el cuello del tapón y el de la botella y la posterior dilatación de dicho tapón por efecto de la humedad, hace que la unión entre estos elementos sea muy sólida, de manera que a pesar de la existencia de la cabeza exterior del tapón, que permite un accionamiento manual y directo sobre el mismo, las maniobras de extracción del tapón resulten extremadamente dificultosas.

Por la propia naturaleza del tapón, es decir por ser éste de madera, imposibilita la utilización de los sacacorchos convencionales, todos los cuales están concebidos para penetrar de una u otra manera en el seno del material constitutivo del tapón.

Descripción de la invención

Problema técnico y solución planteada

Ventaja técnica que aporta la invención

El sacacorchos que la invención propone ha sido específicamente concebido para permitir una fácil extracción de estos tapones de madera. Para ello y de forma más concreta dicho sacacorchos se materializa en un cuerpo que configura un casquillo cilíndrico, dimensionalmente adecuado a la cabeza del tapón, preferentemente con una de sus embocaduras ligeramente estrangulada para constituir un tope limitador de penetración del casquillo en la cabeza del tapón, y con una cota axial igual o inferior a la de dicha cabeza, emergiendo radialmente de dicho cuerpo un brazo de apreciable longitud, mientras que en oposición diametral a dicho brazo y coaxialmente con el mismo incorpora un orificio prolongado exteriormente en un pequeño cuello interiormente roscado, en el que juega el extremo roscado de un segundo brazo, coaxial con el primero y rematado por su otro extremo en una expansión transversal en funciones de asidero, para suministrar al segundo brazo un movimiento giratorio.

De acuerdo con esta estructuración y en situación de retracción para el segundo brazo, en el que éste deja totalmente libre el interior del cuerpo o casquillo, dicho cuerpo resulta fácilmente acoplable a la cabeza del tapón, para seguidamente actuar en sentido giratorio sobre el asidero del segundo brazo provocando el desplazamiento axial del mismo, con penetración en el seno del cuerpo o casquete, incidiendo lateralmente sobre dicha cabeza, es decir actuando a modo de un tornillo prisionero, que fija rigidamente el sacacorchos en su conjunto al tapón, y que permite una fácil extracción de este último suministrándole un movimiento combinado de giro y tracción axial mediante accionamiento de los dedos de la mano simultáneamente sobre ambos brazos del sacacorchos.

Descripción de los dibujos

Explicación detallada de los dibujos

Para complementar la descripción que se está realizando y con objeto de ayudar a una mejor comprensión de las características del invento, de acuerdo con un ejemplo preferente de realización práctica del mismo, se acompaña como parte integrante de dicha descripción, un juego de dibujos en donde con carácter ilustrativo y no limitativo, se ha representado lo siguiente:

La figura 1.- Muestra, según una vista en perspectiva, un sacacorchos realizado de acuerdo con el objeto de la presente invención.

La figura 2.- Muestra un detalle en planta y en sección longitudinal del sacacorchos de la figura anterior.

La figura 3.- Muestra una vista en alzado lateral y también en sección del mismo sacacorchos, ahora en situación de uso, es decir acoplado a un tapón de madera.

La figura 4.- Muestra, finalmente, una representación esquemática en perspectiva de una variante de realización práctica para el sacacorchos.

A la vista de las figuras reseñadas, en especial de las figuras 1 a 3, puede observarse como el sacacorchos que la invención propone está constituido a partir de un cuerpo central (1), que configura un casquillo cilíndrico, de diámetro interno ligeramente superior a diámetro externo de la cabeza (2) del tapón de madera al que se destina, y con una de sus embocaduras provista de una ligera estrangulación (3) en funciones de tope limitador de penetración para la cabeza (2) del tapón, tal como se desprende de la observación de la figura 3.

El cuerpo (1) incorpora exteriormente, como prolongación lateral y monopieza del mismo, un brazo (4) de apreciable longitud, mientras que oposición diametral a dicho brazo cuenta con un orificio (5), coaxial con el brazo (4) y prolongado exteriormente en un pequeño cuello (6) dotado interiormente de una rosca (7) que o bien afecta también al orificio (5) o bien dicho orificio presenta un diámetro ligeramente mayor que el del cuello (6).

A través de la rosca (7) del cuello (6) el sacacorchos recibe a un segundo brazo (8) provisto en uno de sus extremos de un tramo (9) roscado en correspondencia con el cuello (6) y rematado por su otro extremo en una expansión transversal (10) en funciones de asidero, así como de abridor de chapas, que en el ejemplo de realización práctica elegido adopta una configuración anular plana, pero que puede adoptar cualquier otra configuración, acorde con cualquier línea de diseño, sin que ello afecte en absoluto a la esencia de la invención.

De acuerdo con la estructuración descrita y como ya se ha dicho con anterioridad, cuando el extremo roscado (9) del segundo brazo (8) deja libre el interior del cuerpo (1), éste es fácilmente acoplable a la cabeza (2) del tapón, tal como muestra la figura 3, y tras dicho acoplamiento basta con suministrar a la expansión extrema (10) un movimiento giratorio que provoca un cierto desplazamiento axial del eje (8), a través de la rosca (7), con la consecuente penetración del mismo en el interior del cuerpo o casquillo (1) y con la consecuente presión radial sobre la cabeza (2) del tapón, que queda así inmovilizada al sacacorchos, y en condiciones de efectuar la extracción del tapón, traccionando simultáneamente con la mano sobre ambos brazos (4) y (8), preferentemente con un movimiento combinado de basculación lateral para dichos brazos.

De acuerdo con la variante de realización mostrada en la figura 4, el cuerpo (1) puede incorporar su brazo (4') como prolongación axial del mismo, en lugar de adoptar una disposición radial como en el caso anterior, estando este brazo (4') reforzado en su zona de unión al cuerpo (1) mediante una expansión tronco-cónica (11) y rematándose por su extremidad libre en una expansión transversal (12), a modo de "T" y en funciones de asidero.

A continuación se presenta un ejemplo de los dibujos para una solicitud de patente:

EJEMPLO DE LAS FIGURAS O DIBUJOS

