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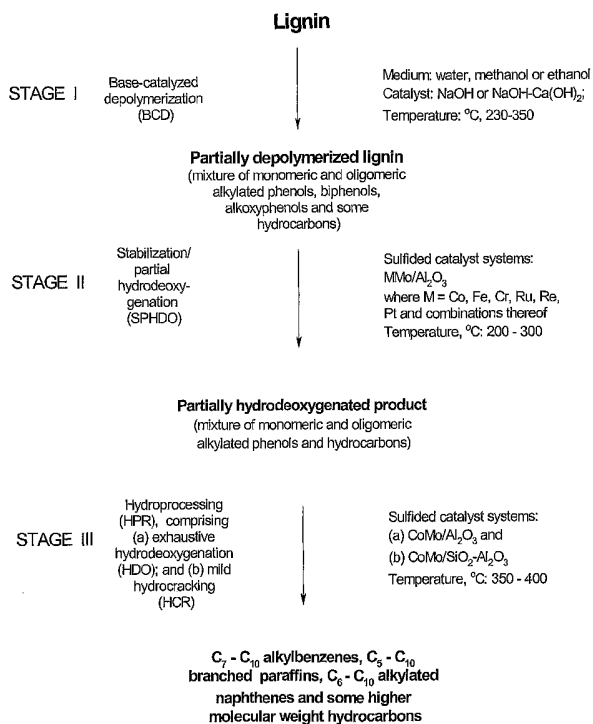
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- (71) Applicant (for all designated States except US): UNIVERSITY OF UTAH RESEARCH FOUNDATION [US/US]; 615 Arapeen Drive, Suite 310, Salt Lake City, Utah 84108 (US).
- (72) Inventors; and
- (75) Inventors/Applicants (for US only): ZMIERCZAK, Wlodzimierz, W. [US/US]; 850 South Donner Way, Apt. 406, Salt Lake City, Utah 84108 (US). MILLER, Jan, D.
- (74) Agents: WESTERN, M., Wayne et al.; THORPE NORTH & WESTERN, LLP, P.O. Box 1219, Sandy, Utah 84091-1219 (US).
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(54) Title: PROCESSES FOR CATALYTIC CONVERSION OF LIGNIN TO LIQUID BIO-FUELS



(57) Abstract: Processes for conversion of lignin to liquid products such as bio-fuels and fuel additives are disclosed and described. A process for conversion of a lignin material to bio-fuels can include subjecting the lignin material to a base catalyzed depolymerization reaction to produce a partially depolymerized lignin. The partially depolymerized lignin can then be subjected to a stabilization/partial hydrodeoxygenation reaction to form a partially hydrodeoxygenated product. Following partial hydrodeoxygenation, the partially hydrodeoxygenated product can be reacted in a refining step to form a bio-fuel. Each of these reaction steps can be performed in single or multiple steps, depending on the design of the process. The production of an intermediate partially hydrodeoxygenation product and subsequent reaction thereof can significantly reduce or eliminate reactor plugging and catalyst coking. A variety of useful bio-fuels such as fuels, fuel additives, and the like can be readily produced from renewable lignin materials in an improved conversion process.

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PROCESSES FOR CATALYTIC CONVERSION OF LIGNIN TO LIQUID BIO-FUELS

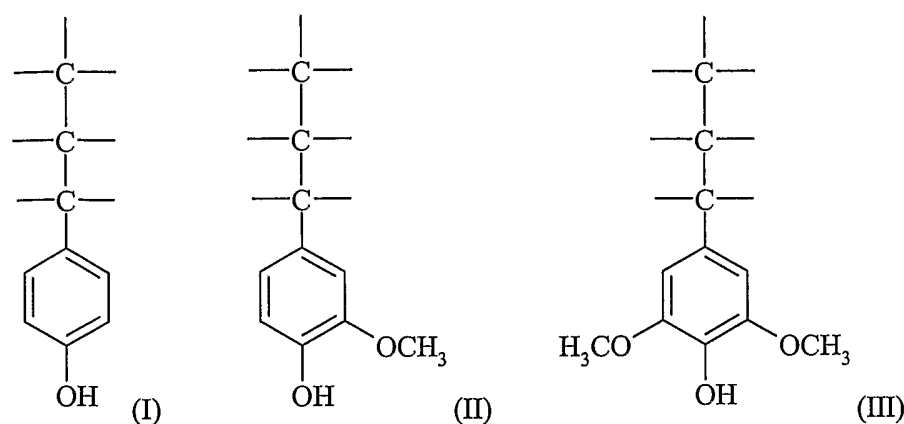
FIELD OF THE INVENTION

The present invention relates generally to conversion of biomass to fuels, fuel additives, and other commercially useful products. More particularly, the present invention relates to a multi-step catalytic process for production of hydrocarbon products from lignin.

BACKGROUND OF THE INVENTION

The current market for energy carriers and fuels is largely driven by high prices of petroleum and natural gas resulting from a depletion of easily accessible deposits, a growing demand caused by the development of new emerging market economies, and mounting environmental concerns. Consequently, these increasing energy demands will require a significant restructure and/or a replacement of a major portion of fossil fuels by renewable energy technologies such as biomass-based energy technologies. Mature technologies are available for the production of a variety of bio-commodities including transportation fuels and chemical building blocks from wood, agricultural crops, municipal solid wastes, landfill gas, *etc.*, which will enable this new energy sector to evolve. This emerging sector serves as a network of bio-refineries (petrochemical refinery analogs) and represents an integrated, environmentally sound processing group of facilities. In these facilities biomass components are separated and converted into valuable intermediates and final products, including bio-fuels, bio-power, and other bio-products.

Cellulose and lignin represent two of the most prominent renewable carbon sources. Lignin, a second to cellulose as the most plentiful renewable carbon source on Earth, is an amorphous three-dimensional energy-rich phenolic biopolymer, which is deposited in all vascular plants and provides rigidity and strength to their cell walls. The lignin polymeric structure is composed primarily of three phenylpropanoid building units: p-hydroxyphenylpropane (Structure I), guaiacylpropane (Structure II), and syringylpropane (Structure III) interconnected by etheric and carbon-to-carbon linkages. Generally, in unprocessed lignins, two thirds or more of these linkages are ether bonds, while the remaining linkages are carbon-carbon bonds.



Different types of lignin differ significantly in the ratio between these monomers. Inherent in its molecular nature, the lignin bio-mass component can potentially be converted directly to liquid fuels, *e.g.*, high-octane alkylbenzene and/or aromatic ether gasoline-blending components.

Currently, a limited supply of lignin is available as a by-product of the pulp and paper industry. However, in the near future, large quantities of lignin residue material will be available from biomass-to-ethanol processes and other biorefineries and associated processes. So far, in typical biorefinery process designs, lignin appears as a residual material with limited opportunities for its utilization. Other sources of lignin material can include agricultural products and wastes, municipal wastes, and the like.

Upgrading of the lignin residue by a catalytic conversion process to high-value fuels and fuel additives have been sought to enhance the competitiveness of biorefinery technologies. Numerous efforts on lignin conversion have included a number of single stage processing methods including hydrocracking, cracking, hydrogenation, hydrotreating, liquefaction in hydrogen-donor solvents, and the like. However, to date, these approaches have achieved limited success for a variety of reasons.

During the past few years several studies have been initiated to develop two-stage processes for making liquid fuels and fuel additives from lignin. These studies provided significant initial groundwork in identifying commercially useful processes for the conversion of lignin to valuable high-octane bio-fuels. Two methods are of particular interest and are described in U.S. Patent Nos. 5,959,167 and 6,172,272, each of which are incorporated herein by reference in their entireties.

One of these methods is described as a lignin-to-gasoline (LTG) two-stage process. A first step involves base-catalyst depolymerization (BCD) of lignin feed in a reaction medium such as an alcohol followed by catalytic hydroprocessing (HPR). In the BCD stage of the

process, lignin is partially depolymerized, mostly by solvolysis of etheric linkages, to ether-soluble mono-, bi- and trimeric phenolic units, and some hydrocarbons. In the second stage of the procedure, hydroprocessing (HPR), the BCD product is subjected to simultaneous hydrodeoxygenation (HDO) and hydrocracking (HCR) for complete removal of remaining oxygen and to break the inter-aromatic C – C linkages. The overall BCD-HPR procedure yields a low-sulfur, high-octane hydrocarbon gasoline additive consisting of a mixture of C₇ - C₁₁ alkylbenzenes, and some C₆ - C₁₁ mono-, di-, tri- and polyalkylated naphthenes and C₅ - C₁₁ (mostly multi-branched) paraffins.

The second two-stage method is a lignin-to-aromatic ethers (LTE) process and was designed primarily for production of partially oxygenated gasoline or for the selective production of C₇ - C₁₁ methoxybenzenes as high-octane additives. This process uses a similar two-stage procedure as the first process briefly described above. In the first stage, lignin is subjected to a mild base-catalyst depolymerization (BCD) in supercritical alcohol as a reaction medium. This step is then followed by non-deoxygenative hydrotreatment/mild hydrocracking (HT), and a subsequent etherification (ETR) of the intermediate phenolic product to yield a reformulated, partially oxygenated gasoline. The resulting gasoline is typically a mixture of (substituted) phenyl methyl ethers (blending octane number, 124 - 166; boiling point, 154 - 195 °C) and cycloalkyl methyl ethers, C₇ - C₁₀ alkylbenzenes, C₅ - C₁₀ (mostly multi-branched) paraffins, and polyalkylated cycloalkanes.

Unfortunately, these two-stage processes can suffer from excessive catalyst coking and formation of polymeric solids which tend to clog the reactors. Further, alcohol-based solvents tend to alkylate with the reactants and oxidize to acetic acid which reduces yields and makes disposal of by-products more difficult.

Accordingly, investigations continue into developing processes for conversion of lignin to more valuable products that are economically viable. Many challenges still remain to provide useful product yields without sacrificing process reliability.

SUMMARY OF THE INVENTION

It has been recognized that it would be advantageous to develop processes which allow for conversion of lignin to more valuable products such as bio-fuels and fuel additives with improved yields and acceptable processing conditions.

In accordance with one aspect of the present invention, a process for conversion of a lignin material to bio-fuels can include subjecting the lignin material to a base catalyzed depolymerization reaction to produce a partially depolymerized lignin. The partially

depolymerized lignin can then be subjected to a stabilization/partial hydrodeoxygenation reaction to form a partially hydrodeoxygenated product. Following hydrodeoxygenation, the partially hydrodeoxygenated product can be reacted in a refining step to form a bio-fuel. Each of these reaction steps can be performed in single or multiple steps, depending on the design of the process.

In one detailed aspect of the present invention, the based catalyzed depolymerization reaction can include dissolving the lignin material in an aqueous base catalyst in the presence of a polar solvent. The dissolved lignin material can then be subjected to reaction conditions sufficient to partially depolymerize the lignin material. The partially depolymerized phenolic lignin products can be recovered and optionally separated from other products as a part of the based catalyzed depolymerization reaction.

In a more detailed aspect, the base catalyst can be NaOH, KOH, Ca(OH)₂, Mg(OH)₂, and mixtures thereof, although other base catalysts could be used. Similarly, a number of polar solvents can be used; however, water is currently preferred. Further, in one aspect, the base catalyzed depolymerization reaction can be carried out under conditions which are substantially free of alcohols.

In another detailed aspect, the stabilization/partial hydrodeoxygenation reaction can include exposing the partially depolymerized lignin to a solid catalyst at a temperature below about 300 °C, e.g., from about 200 °C to about 300 °C.

A variety of solid catalysts can be useful for the stabilization/partial hydrodeoxygenation reaction. Typically, the solid catalyst can include a support material and a catalyst material. Preferably, the support material can be a non-acidic material such as activated carbon, silicon dioxide, aluminum oxide, or combinations thereof. The choice of material for the catalyst material portion of the solid catalyst can also be an important consideration. Non-limiting examples of particularly suitable catalyst material can include Co-Mo, Rh-Mo, Ru-Mo, Pt-Mo, Pd-Mo, and combinations, alloys or composites thereof.

In another detailed aspect of the present invention, the stabilization/partial hydrodeoxygenation reaction can occur at conditions sufficient to convert greater than about 95%, and preferably greater than about 98%, of methoxyphenols and benzenediols to phenol-based products having a single oxygen moiety.

Still another aspect of the present invention includes performing any number of refining steps designed to achieve a particular bio-fuel product. For example, the refining step can include a hydrodeoxygenation reaction, a mild hydrocracking reaction, an etherification reaction, a hydrogenation reaction, and/or combinations thereof.

The refining step can be a hydroprocessing reaction which includes a hydrodeoxygenation step and a subsequent hydrocracking step. Although process conditions can vary, the hydroprocessing reaction can occur at a temperature from about 250 °C to about 400 °C, and in some cases from about 320 °C to about 450 °C.

Alternatively, the refining step can include a mild hydrocracking reaction followed by an etherification reaction.

In yet another alternative embodiment, the partially hydrodeoxygenated product can be fractionated into a first monomeric fraction and a second oligomeric fraction (e.g., dimers, trimers, and heavily substituted rings). The first low molecular weight fraction can be treated in an etherification reaction with methanol or ethanol to form aromatic ethers which are particularly useful as fuel additives. Similarly, the second high molecular weight alkylphenol fraction can then be treated in a hydroprocessing reaction and an optional hydrogenation reaction to form bio-fuels such as aromatic gasolines and/or jet fuels.

Additional features and advantages of the invention will be apparent from the detailed description which illustrates, by way of example, features of the invention.

BRIEF DESCRIPTION OF THE DRAWINGS

Aspects of the invention can be better understood with reference to the following drawings.

FIG. 1 is a flow diagram of a three stage process for conversion of lignin to alkylbenzene gasoline blending components in accordance with an embodiment of the present invention.

FIG. 2 is a flow diagram of a four stage process for conversion of lignin to aromatic ether gasoline blending components in accordance with an embodiment of the present invention.

FIG. 3 is a flow diagram of an integrated process for conversion of lignin to liquid transportation fuels in accordance with another embodiment of the present invention.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENT(S)

Before particular embodiments of the present invention are disclosed and described, it is to be understood that this invention is not limited to the particular process and materials disclosed herein as such may vary to some degree. It is also to be understood that the terminology used herein is used for the purpose of describing particular embodiments only

and is not intended to be limiting, as the scope of the present invention will be defined only by the appended claims and equivalents thereof.

In describing and claiming the present invention, the following terminology will be used.

The singular forms "a," "an," and "the" include plural referents unless the context clearly dictates otherwise. Thus, for example, reference to "a step" includes reference to one or more of such steps.

As used herein, "reaction" is intended to cover single step and multi-step reactions which can be direct reactions of reactants to products or may include one or more intermediate species which can be stable or transient.

As used herein, "bio-fuels" refers to any fuel, fuel additive, aromatic, and/or aliphatic compound derived from a biomass starting material such as lignin.

As used herein, "lignin" and "lignin material" are used interchangeably and refer to a biomass material which is an amorphous three-dimensional energy-rich phenolic biopolymer. Lignin is typically deposited in nearly all vascular plants and provides rigidity and strength to their cell walls. As mentioned above, the lignin polymeric structure is composed primarily of three phenylpropanoid building units interconnected by etheric and carbon-to-carbon linkages. Non-limiting examples of lignin material can include agricultural lignin, wood lignin, lignin derived from municipal waste, Kraft lignin, organosolve lignin, and combinations thereof. Wood lignin is currently a widely available and renewable resource which can be particularly suitable for use in the present invention.

As used herein, "oxygen moiety" refers to any oxygen-containing substituent to an aromatic ring or other main group. Typically, oxygen moieties present on the compounds of the present invention can include hydroxyl groups, however other groups such as methoxy, alkoxy, carboxy, and the like can also be included. Compounds containing a single oxygen moiety are stabilized, or in other words, are not polymerizable under identified process conditions, e.g. phenol or other aromatics containing a single oxygen moiety. In contrast, compounds containing two or more oxygen moieties tend to be polymerizable to form undesirable coking, e.g. methoxyphenol, benzenediol, and the like.

As used herein, "non-acidic support material" refers to a solid catalyst support which is non-acidic. In terms of a solid, the terms pH and pKa are generally unhelpful because these terms are measures of fluid conditions. As such, the acidity of a solid can be measured as a complex function expressed as a Hammett indicator. Actual Hammett indicator values for the catalyst support materials of the present invention are currently unknown. However, in the context of the present invention, non-acidic support materials for SPHDO

(stabilization/partial hydrodeoxygenation) are those which are substantially free of acidic sites sufficient to avoid poisoning by coking. Conventional catalyst support materials are most often provided as acidic support materials; however, non-acidic support materials can be formed or prepared by adjusting the method of preparation, subsequent treatment with bases or other available methods to remove or neutralize any acidic sites. For example, alumina support materials can be acidic or non-acidic depending on the method of preparation or subsequent treatments.

As used herein, "substantial" when used in reference to a quantity or amount of a material, or a specific characteristic thereof, refers to an amount that is sufficient to provide an effect that the material or characteristic was intended to provide. The exact degree of deviation allowable may in some cases depend on the specific context. Similarly, "substantially free of" or the like refers to the lack of an identified element or agent in a composition. Particularly, elements that are identified as being "substantially free of" are either completely absent from the composition, or are included only in amounts which are small enough so as to have no measurable effect on the composition.

As used herein, the terms "partial" or "partially" when used in connection with the phrase "stabilization/partial hydrodeoxygenation" or "SPHDO" refer to the percentage of oxygen moieties eliminated from the end products of the base-catalyzed depolymerization (BCD) reaction of lignin. The percentage of the total oxygen removed from the BCD end product can range from 30% to 60%, and preferably average about 50%. As such, more than about 95% and preferably more than about 99% of polymerizable BCD end products (i.e. products having multiple oxygen moieties) can be converted to stabilized products having single oxygen moieties. The "partial" hydrodeoxygenation occurs when the methoxy and/or hydroxyl groups are removed from methoxyphenol or benzenediol compounds to yield single oxygen containing phenolic compounds.

As used herein, "refining step(s)" refers to any single reaction or combination of reactions or reaction steps which processes the partially hydrodeoxygenated products of the SPHDO reaction into a biofuel. Examples of refining steps include but are not limited to hydroprocessing reactions such as hydrodeoxygenation reactions, mild hydrocracking reactions, etherification reactions, hydrogenation reactions, and combinations thereof.

As used herein, a plurality of items, structural elements, compositional elements, and/or materials may be presented in a common list for convenience. However, these lists should be construed as though each member of the list is individually identified as a separate and unique member. Thus, no individual member of such list should be construed as a de

facto equivalent of any other member of the same list solely based on their presentation in a common group without indications to the contrary.

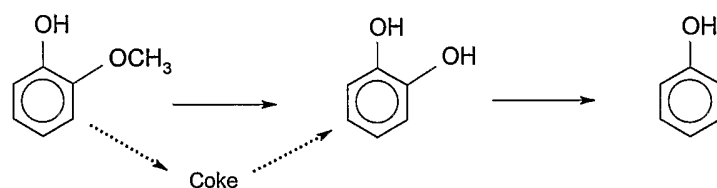
Concentrations, amounts, and other numerical data may be presented herein in a range format. It is to be understood that such range format is used merely for convenience and brevity and should be interpreted flexibly to include not only the numerical values explicitly recited as the limits of the range, but also to include all the individual numerical values or sub-ranges encompassed within that range as if each numerical value and sub-range is explicitly recited. For example, a weight range of about 1% to about 20% should be interpreted to include not only the explicitly recited concentration limits of 1% to about 20%, but also to include individual concentrations such as 2%, 3%, 4%, and sub-ranges such as 5% to 15%, 10% to 20%, etc.

In accordance with the present invention, bio-fuels can be produced using a three-step process including based-catalyzed depolymerization, stabilization/ partial hydrodeoxygenation, and a refining step. In previous approaches, subsequent steps of both, the LTG (U.S. Patent No. 5,959,167) as well as the LTE (U.S. Patent No. 6,172,272) processes, the BCD product was treated in hydroprocessing (HPR) and selective hydrocracking (HC) steps, respectively, with acidic catalysts at temperatures above 350 °C. This approach can be useful in some circumstances; however, the high temperatures required can result in a reduction in reliability during scale-up and extended production runs. This application is related to U.S. Provisional Patent Application Serial No. 60/677,662, filed on May 2, 2005, which is herein incorporated in by reference.

Typically, lignin BCD products are primarily phenolic compounds including mono-, di-, and polyalkylated phenols, methoxyphenols, benzenediols, and some polyalkylated benzenes (e.g. 2-10%), and dimeric and trimeric aromatic non-phenolic compounds. Such a product, if used in the LTG process, requires further upgrading, e.g., removal of oxygen via a hydrodeoxygenation process and a simultaneous (using a hybrid catalyst) or consecutive hydrocracking, which results in a higher chemical stability and increases H/C ratio, heating value, *etc.* The BCD process tends to produce a relatively high content of very reactive, thermally unstable methoxyphenols and benzenediols. These unstable phenols tend to undergo rapid polycondensation that results in solid plugs in the HDO reactors during high-temperature (> 300 °C) HDO process. Moreover, a relatively strong interaction of these compounds with typical HDO catalyst support acid sites (on alumina and other acidic supports), results in significant catalyst coking. Additionally, the presence of a strongly acidic hydrocracking (HCR) co-catalyst component results in fast catalyst coking and

subsequent deactivation of the HCR catalyst. Similar conditions were observed in the MH step of the LTE process.

In accordance with the present invention, a low temperature stabilization/partial hydrodeoxygenation (SPHDO) treatment can be considered preceding the HPR process in order to alleviate the problem of catalyst deactivation and repolymerization. Typically, SPHDO treatment can be performed at a low temperature range (e.g. 200 °C – 400 °C, and often less than about 300 °C, depending on the catalyst); however, other temperature ranges can be suitable depending on the catalyst and associated reaction kinetics. The SPHDO treatment process can result in conversion of methoxyphenols to benzenediols and methane, and then subsequently eliminate one OH group from benzenediols to produce phenols. Further, elimination and/or reduction of acid sites on surfaces of an SPHDO catalyst support can prevent undesirable coke buildup. As illustrated in Equation I, a reaction scheme for partial hydrodeoxygenation/stabilization of guaiacol (2-methoxyphenol) is shown.



(Equation I)

The bond dissociation energy of the oxygen atom attached to aromatic carbons in phenols and ethers is about 84 kJ/mol greater than that of an oxygen atom attached to aliphatic carbons. This can at least partially explain why removal of a methyl group from a methoxy group is easier than removal of entire methoxy groups. Production of methane is quite low and is dominantly CO₂, with some H₂ and hydrocarbons. This product can be useful as a fuel source and can be combusted on site as an additional heating source. The partial hydrodeoxygenation/stabilization reactions of the present invention can act to remove polymerizable moieties to reduce or prevent undesirable polycondensation products from forming.

The resulting SPHDO phenolic products can then be subjected to a variety of refining steps such as hydroprocessing (HPR) without formation of substantial polycondensation products. Thus, the SPHDO step can allow for reduced catalyst coking, reduced reaction temperatures and reduced costs, as well as allow subsequent high-temperature (>300 °C) hydroprocessing (HPR), i.e. substantially complete hydrodeoxygenation (HDO) and hydrocracking (HCR) to break interaromatic C – C linkages. HDO and HCR reactions can be

carried out either separately or in a single processing step. Careful selection of HDO and HCR catalysts and process conditions is desirable for selective conversion of BCD-SPHDO product to a monomeric, mostly aromatic product. As a general matter, HDO catalysts can be chosen based on low hydrogenation activity and HCR catalysts based on optimizing acidity and low hydrogenation activity. Aromatic ring hydrogenation during these reactions should be minimized by careful choice of the catalyst and associated temperatures.

In accordance with the present invention, particular attention can be given to preparing effective SPHDO catalysts possessing high activity and resistance to the deactivation effects. In one aspect, a SPHDO catalyst can be prepared by altering typical HDO catalysts. For example, an acidic alumina support can be replaced with alternative, non-acidic supports such as non-acidic alumina (neutralized with NaOH, KOH, etc.), active carbon, silica, and composites thereof. Alternatively, or in addition to the above, noble metals can be incorporated into the active phase of the catalyst. In yet another alternative, SPHDO catalysts such as supported or unsupported transition metal nitrides and carbides can be useful. Non-limiting examples of suitable SPHDO catalysts can include but are not limited to supported or unsupported transition metal nitrides, supported or unsupported transition metal carbides, or combinations thereof. Examples of transition metal nitrides include but are not limited to VN; Mo₂N, TiN, and combinations thereof. Examples of transition metal carbides include but are not limited to WC, Mo₂C, VC, and combinations thereof. As a catalyst for SPHDO step, the acidity can be one important factor in determining effectiveness. In particular, SPHDO catalyst support materials can be non-acidic such that the reaction kinetics of the catalytic stabilization reactions are controlling over non-catalytic repolymerization and coking reactions. As temperatures increase, the non-catalytic coking reactions tend to become controlling. For example, CoMo/Al₂O₃ SPHDO non-acidic catalysts typically have a maximum operating temperature of about 300 °C before non-catalytic coking reactions become controlling which leads to poisoning of the catalyst. Other SPHDO catalysts and temperature conditions may vary. However, at least some minor repolymerization reactions can be desirable as such species in minor amounts can act as catalytic promoters for the desirable SPHDO oxygen-group elimination reactions.

Noble metal-containing catalysts are generally more active and selective for SPHDO than standard HDO catalysts. Another important advantage of these catalysts is their ability to perform selective direct elimination of entire methoxy groups resulting in compounds containing only one atom of oxygen (phenols) as a main product. Furthermore, such catalysts can be less active for unwanted reactions, e.g., coking and aromatic ring hydrogenation. More highly active catalysts can perform acceptably well in a lower temperature range where

coking reactions proceed more slowly. Also, application of active coal or SiO₂ as an SPHDO catalyst support can provide reduced coking. As a general guideline, the SPHDO catalyst and support material can be non-acidic and being substantially free of acidic sites sufficient to avoid poisoning by coking at the specified operating temperatures.

Several examples of specific applications of the present invention are described in detail below with respect to an enhanced catalytic lignin conversion process such as an enhanced lignin-to-gasoline (ELTG) process; an enhanced lignin-to-aromatic ethers (ELTE) process; and an integrated lignin-to-liquid fuels process (ILTF). Each of these processes includes the same basic lignin conversion stages, e.g., BCD and SPHDO. Specific operating conditions and additional further stages such as refining steps can depend on the desired product.

Enhanced Lignin-to-Gasoline (ELTG) Process

A flow diagram of the proposed the enhanced lignin conversion process for production of aromatic gasoline and gasoline additives, in a three-stage procedure is presented in FIG. 1. In the first stage of the process, a lignin feed is subjected to base-catalyzed depolymerization (BCD) to form a partially depolymerized product. In the second stage, the partially depolymerized BCD product can be subjected to a low temperature stabilization/partial hydrodeoxygenation (SPHDO) process. During the third stage of the process, the SPHDO product can be hydroprocessed to obtain a bio-fuels product including aromatic-rich gasoline and a higher molecular weight fraction. The specific bio-fuel product composition can strongly depend on the HPR processing conditions. The latter fraction can be optionally subjected to exhaustive aromatic ring hydrogenation to obtain valuable naphthenic kerosene (NK). Each of these three steps is discussed in more detail below.

In the first stage of the process a lignin material can be dissolved in an aqueous base-catalyst solution. Although specific process conditions can vary, typical reaction temperatures can range from about 230 °C to about 350 °C. Similarly, autogenic pressure of from about 1000 to about 2300 psig can be useful. The BCD reaction can generally be operated at a lignin material feed rate in liquid hourly space velocity (LHSV) of about 0.5 to about 6.0 hr⁻¹. Alkali and alkaline earth metal hydroxides can be used as base catalysts. Non-limiting examples of suitable base catalysts can include NaOH, KOH neat, Ca(OH)₂, Mg(OH)₂, and mixtures thereof. In one aspect, the preferred liquid medium is water; however, methanol and/or ethanol can also be used, as well as combinations of water, methanol, and/or ethanol.

Preferably, a continuous stirred-tank reactor (CSTR) can be used in connection with the BCD process. However, any reactor which reduces or eliminates accumulation of precipitates can be used, e.g., any agitated reactor, and the like. Precipitates can appear in connection with reduction in the base catalyst concentration during the BCD process and can also cause reactor plugging.

The primary solid/liquid portion of the BCD reaction product can be precipitated by acidification with CO₂ and/or other acidic species such as, but not limited to, hydrochloric acid, sulfuric acid, phosphoric acid, and the like. As an added benefit, washing with phosphoric acid can also result in a fertilizer by-product. The precipitated BCD product can then be washed and dried. The remaining non-precipitated BCD water-soluble product (mostly benzenepolyols such as benzenediol) can be extracted from the water solution with diethyl ether and added to the acid-precipitated water-insoluble primary portion of the product. Alternatively, the extracted water soluble BCD product can be used as a source of valuable bio-chemicals as is. The dry BCD product can be diluted at a temperature range of about 100 °C to about 150 °C with any number of liquid vehicles such as self-produced, selected fractions of SPHDO and/or HPR products. Insoluble high-molecular weight components can be separated by filtration or centrifugation and desalted. These insoluble components can be used as feed in the SPHDO process. A suitable desalting treatment similar to those applied in crude oil treatment can be useful to prevent corrosion and catalyst poisoning effects by sodium and calcium salts occluded in the solid BCD product. In yet another alternative, diluted ether-extracted low-molecular weight fraction of the BCD product can be used as feed in the SPHDO process.

During the initial period of the previous studies of the partial base catalyzed depolymerization (BCD) of lignin the catalyst examined in the process was NaOH (KOH and CsOH were also tested), whereas supercritical methanol or ethanol were used as solvents and reaction media. Batch reactor experiments with alcoholic solvents have shown a high degree of lignin depolymerization (up to 98 wt% of an ether-soluble product). However, during the BCD process, extensive ring methylation (ethylation), and partial conversion of methanol and ethanol to formic and acetic acids, respectively, took place. These reactions resulted in formation of undesirable higher molecular weight ($\geq C_9$) phenols, and loss of an alcoholic solvent due to neutralization of the base catalyst with the emerging acids. This resulted in relatively high catalyst/lignin ratio in order to obtain a high level of depolymerization of lignin. To eliminate these problems and improve the economy of the process, alcoholic solvents were replaced with water as an inert, non-alkylating, and cheaper solvent.

Using a packed flow reactor system, water as a solvent, and NaOH as a catalyst, lignin can be converted up to 60 - 80 wt% of ether-soluble product at moderate temperature and short reaction times. Experiments using an NaOH-Ca(OH)₂ (low NaOH concentration) system in a batch microreactor showed significant resistance to NaOH catalyst neutralization. In addition, Ca(OH)₂ contributes mainly in the BCD reaction as CO₂ and weak organic acid scavenger.

The hydrolysis of etheric linkages in the lignin structure in the BCD process results in the formation of significant amounts of monomeric phenols and benzenediols and alkoxyphenols which are also valuable chemical co-products.

The partially depolymerized lignin BCD product or its ether extract, after it is diluted with a part of the fraction of the self-produced phenolic and/or high boiling alkylaromatic product, can be subjected to a low temperature stabilization/partial hydrodeoxygenation (SPHDO) process. This process can include the conversion of unstable methoxyphenols and benzenediols to a stable phenolic product on catalysts such as those discussed herein such as CoMo catalysts supported on alumina and active carbon. These catalysts can also be used in the basic form, as well as those modified by neutralization of the support surface acidity (alumina) and/or introduction of additional noble metal promoters such as Pt, Pd, Ru, and Rh.

Currently preferred catalysts of this type are sulfided, noble metal-promoted MMo/C systems, where M = Rh, Ru and Pt. Sulfiding of catalysts can be carried out by treatment with a mixture of hydrogen and hydrogen sulfide. These noble metal-containing catalysts demonstrate high HDO activity and superior selectivity to phenols. An important element of carbon-supported catalyst is the low cost of the carbon support and the ability of recovering the precious metals from spent catalysts by simply burning off the carbon, rather than more expensive refining or recovery processes.

The currently preferred processing conditions for the SPHDO reaction are a temperature from about 200 °C to about 300 °C, a residence time of about 5 to about 15 minutes, and H₂ pressure from about 500 to about 2000 psig. Although not required, the entire volume of SPHDO product is typically subjected to the refining step of hydroprocessing (HPR).

The HPR reaction runs with the BCD-SPHDO product as feed can be carried out in a single step procedure, or as a sequence of separate HDO and HCR reactions to obtain an aromatic-rich product, consisting mostly of C₇ - C₁₁ alkylbenzenes. HDO (CoMo/Al₂O₃) and HCR (CoMo/Al₂O₃-SiO₂ which can be amorphous or crystallized, i.e. zeolite) catalysts are preferred due to their high activity and selectivity in terms of obtaining desirable, mostly

monomeric aromatic, free of oxygen final HPR product. Other useful catalysts can include, but are certainly not limited to, $\text{MMo}/\gamma\text{-Al}_2\text{O}_3$ (HDO) and $\text{MMo}/\text{Al}_2\text{O}_3\text{-SiO}_2$ (HCR), where M = Ru, Re, Cr or Fe (and combinations with Co), as well as carbides and nitrides thereof. This process requires a careful selection of optimum reaction conditions and catalysts to minimize aromatic ring hydrogenation reactions in order to maximize monomeric aromatic compounds that are desirable as a final bio-fuels product of the process of the present invention. The degree of undesirable ring hydrogenation of C_7 - C_{10} alkylbenzenes to corresponding naphthenes is readily controllable by processing conditions and can be minimized or even substantially eliminated.

Careful selection of HDO and HCR catalysts and process conditions is desirable for selective conversion of BCD-SPHDO product to a monomeric, mostly aromatic product. As a general matter, HDO catalysts can be chosen based on low hydrogenation activity and HCR catalysts based on optimizing acidity and low hydrogenation activity. Aromatic ring hydrogenation during these reactions should be minimized by careful choice of the catalyst and associated temperatures. For example, using Ni in an HDO catalyst is highly active but also tends to result in high yields of cyclohexane and other hydrogenated products. Generally, HDO catalysts can be neutral, slightly acidic or even slightly basic with substantially neutral being preferred. Specifically, the HDO catalysts can be chosen to allow exhaustive hydrodeoxygenation without poisoning by coking. In contrast, HCR (or MH) catalysts-support materials are generally acidic or strongly acidic sufficient to provide cracking without also causing excessive coking.

Higher molecular weight fraction components such as alkylated naphthalenes, alkylated tetralines, alkylated indanes, alkylated biphenyls and polyalkylated benzenes of the BCD-SPHDO-HPR product (b.p. > 205 °C) can be optionally subjected to exhaustive hydrogenation, yielding high-value naphthenic kerosene as shown in Stage III of FIG. 1.

Enhanced Lignin-to-Aromatic Ethers (ELTE) Process

Referring now to FIG. 2, the BCD and SPHDO stages of the ELTE process can be nearly the same as presented for the ELTG process of FIG. 1. The BCD-SPHDO product can be subjected to subsequent mild hydrocracking and etherification with methanol.

As previously observed, the BCD-SPHDO of lignin results in a high-yield but incomplete depolymerization of the feed's polymeric structure. For example, in addition to the main product consisting of monocyclic phenols, there are significant amounts of intermediate phenolic oligomers. To increase the amount of the monomeric product, a mild hydrocracking procedure for the crude BCD product (designated as an MH procedure), in the presence of solid superacid catalysts is shown in FIG. 2 as Stage III. This supplemental MH

treatment can effectively depolymerize the lignin by selective C - C cleavage of residual intermediate oligomers to produce the desirable monomeric phenols. Although processing conditions for the MH treatment can vary, the currently preferred processing conditions are a reaction temperature from about 200 °C to about 400 °C, a residence time from about 5 to about 30 minutes, and a pressure (H_2) from about 1,000 to about 1,800 psig. Non-limiting examples of suitable strongly acidic catalysts for MH treatment step can include $Pt/WO_4^{2-}/ZrO_2$, heteropolyacids and their salts (supported and unsupported), $FeCl_3 \cdot 6H_2O$, and the like.

As shown in FIG. 2 at Stage IV, a mixture of light monomeric phenols in the BCD-SPHDO product can be subjected to etherification with methanol. Preferably, the etherification reaction can be performed at a reactor temperature from about 200 °C to about 400 °C and an autogenous pressure from about 100 to about 2000 psig.

Almost any suitable catalyst can be used in the etherification reaction. Suitable catalysts can include, but are not limited to, supported heteropolyacids or their salts, potassium benzoate, Cs-P/SiO₂, $SO_4^{2-}/MnO_x/Al_2O_3$, $SO_4^{2-}/MoO_x/Al_2O_3$, $SO_4^{2-}/WO_x/Al_2O_3$, $SO_4^{2-}/CrO_x/Al_2O_3$, $SO_4^{2-}/CeO_x/Al_2O_3$, and the like. Typically, methanol can be used as the etherification agent. Any flow reactor system which allows for continuous drying of the recycled reaction mixture can be used.

The ELTG process of the present invention provides a number of benefits over previously available processes. The majority portion of oxygen present in the BCD-SPHDO product can be preserved which eliminates the need for costly further hydrodeoxygenation steps. Additionally, oxygen remains incorporated in a major portion of the final, high-octane alkoxybenzene gasoline components. Therefore, there is substantially no need for outside oxygen-containing additives, as recommended by the Clean Air Act amendment. Also, the final total ELTG product, including hydrocarbons, is expected to have octane numbers of about 130. As a result, these products can be conveniently used as a blending additive (e.g. to petroleum-derived gasolines having lower octane numbers) to generate premium reformulated gasolines possessing greatly improved combustion characteristics.

Integrated Lignin-to-Liquid Fuels (ILTF) Process

In another aspect of the present invention, the ELTG and ELTE processes can be integrated into a single process. The final ILTF products derived from such an integrated process can include the products of each of the ELTG and ELTE processes such as alkylbenzene gasoline, aromatic ether gasoline additives, and naphthenic kerosene.

As discussed above in connection with FIGs. 1 and 2, a base catalyzed depolymerization reaction can be used to produce a partially depolymerized lignin product. Preferably, the base catalyzed depolymerization reaction can be performed with substantially only water as the solvent and reaction medium. Following the BCD reaction, a low temperature stabilization/partial hydrodeoxygenation (SPHDO) process and (optional) fractionation of C₆ - C₉ alkylphenols from the SPHDO product can be performed. High-temperature hydroprocessing reactions (HPR) of SPHDO product can yield aromatic-rich gasoline as a primary product. Further, exhaustive hydrogenation of higher molecular weight fraction of the HPR product, containing alkylated naphthalenes, alkylated tetralines, alkylated indanes, alkylated biphenyls and polyalkylated benzenes, yielding high-value naphthenic kerosene. Etherification of C₆ - C₉ alkylphenols from the SPHDO product can be performed to produce aromatic ethers (alkylated alkoxybenzenes). Each of these steps was previously discussed in connection with FIGs. 1 and/or 2.

A flow diagram of the integrated lignin conversion process (ILTF) for production of aromatic gasoline, rocket/jet propellant and aromatic ethers in a multi-stage procedure is presented in FIG. 3. In the first stage of the process, lignin material can be subjected to base-catalyzed depolymerization (BCD) with water, optionally methanol or ethanol, as solvent and reaction medium. The entire partially depolymerized lignin product or its ether extract, after being diluted with a part of SPHDO product and/or the high-boiling fraction of the alkylaromatic product, can be subjected to a low temperature stabilization/partial hydrodeoxygenation (SPHDO) process. This SPHDO process involves the conversion of unstable methoxyphenols and benzenediols to a more stable phenolic product. During a third stage of the process, the partially hydrodeoxygenated SPHDO product can be subjected to hydroprocessing (HPR) reactions in order to obtain aromatic-rich gasoline. Higher molecular weight compounds, e.g., alkylated naphthalenes, alkylated tetralines, alkylated indanes, alkylated biphenyls and polyalkylated benzenes are produced as a hydroprocessing product. The yields and types of products can be controlled to some extent by the HPR process.

The hydroprocessing products can then be optionally subjected to exhaustive catalytic hydrogenation. This hydrogenation step can yield naphthenic kerosene containing a mixture of alkylated decalins, alkylated bicyclohexyls, alkylated hydrindanes, and polyalkylated cyclohexanes. In an optional separate processing approach, C₆ - C₉ alkylphenols fractionated from the SPHDO product can be used as feed for the etherification process with methanol leading to alkoxyphenols.

The integrated ILTF process can lead to production of at least three valuable fuel products, provides an opportunity to perform the overall lignin conversion process in a

feasible way, and can improve the overall economy of the process as well as overall economy of projected bio-refineries.

It is to be understood that the above-referenced arrangements are illustrative of the application for the principles of the present invention. Numerous modifications and alternative arrangements can be devised without departing from the spirit and scope of the present invention while the present invention has been shown in the drawings and described above in connection with the exemplary embodiments(s) of the invention. It will be apparent to those of ordinary skill in the art that numerous modifications can be made without departing from the principles and concepts of the invention as set forth in the claims.

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CLAIMS

What is claimed is:

1. A process for conversion of a lignin material to bio-fuels, comprising:
 - a) subjecting the lignin material to a base catalyzed depolymerization reaction to produce a partially depolymerized lignin;
 - b) subjecting the partially depolymerized lignin to a stabilization/partial hydrodeoxygenation reaction to form a partially hydrodeoxygenated product; and
 - c) reacting the partially hydrodeoxygenated product in a refining step to form a bio-fuel.
2. The process of claim 1, wherein the based catalyzed depolymerization reaction includes dissolving the lignin material in an aqueous base catalyst in the presence of a polar solvent, subjecting dissolved lignin material to reaction conditions sufficient to partially depolymerize the lignin material, and recovering the partially depolymerized lignin.
3. The process of claim 2, wherein the base catalyst is a member selected from the group consisting of NaOH, KOH, Ca(OH)₂, Mg(OH)₂, and mixtures thereof.
4. The process of claim 2, wherein the polar solvent is water.
5. The process of claim 1, wherein the based catalyzed depolymerization reaction occurs at from about 230 °C to about 350 °C.
6. The process of claim 1, wherein the stabilization partial hydrodeoxygenation reaction occurs at from 200 °C to 300 °C.
7. The process of claim 1, wherein the stabilization/partial hydrodeoxygenation reaction occurs at a pressure of 500 psig to about 2000 psig.
8. The process of claim 1, wherein the stabilization/partial hydrodeoxygenation reaction includes exposing the partially depolymerized lignin to a solid catalyst at a temperature below about 300 °C.
9. The process of claim 8, wherein the solid catalyst includes a non-acidic support material and a catalyst material.

10. The process of claim 9, wherein the non-acidic support material is selected from the group consisting of an activated carbon, silicon dioxide, aluminum oxide, or combinations thereof.
11. The process of claim 8, wherein the catalyst material is selected from the group consisting of Co-Mo, Rh-Mo, Ru-Mo, Pt-Mo, Pd-Mo, and combinations thereof.
12. The process of claim 8, wherein the catalyst is supported or unsupported transition metal nitrides or transition metal carbides.
13. The process of claim 12, wherein the supported or unsupported transition metal nitride is selected from the group consisting of VN, Mo₂N, TiN, and combinations thereof.
14. The process of claim 12, wherein the supported or unsupported transition metal carbide is selected from the group consisting of WC, Mo₂C, VC, and combinations thereof.
15. The process of claim 8, wherein the stabilization/partial hydrodeoxygenation reaction occurs at conditions sufficient to convert greater than about 95% of methoxyphenols and benzenediols to phenol-based products having a single oxygen moiety.
16. The process of claim 1, wherein the refining step includes a reaction selected from the group consisting of a hydrodeoxygenation reaction, a mild hydrocracking reaction, an etherification reaction, a hydrogenation reaction, and combinations thereof.
17. The process of claim 1, wherein the refining step is a hydroprocessing reaction including a hydrodeoxygenation step and a subsequent hydrocracking step.
18. The process of claim 17, wherein the hydroprocessing reaction occurs at a temperature from about 320 °C to about 450 °C.
19. The process of claim 16, wherein the refining step is a mild hydrocracking reaction followed by an etherification reaction.

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20. The process of claim 16, further comprising fractionating the partially hydrodeoxygenated product into a first monomeric fraction and a second oligomeric fraction.

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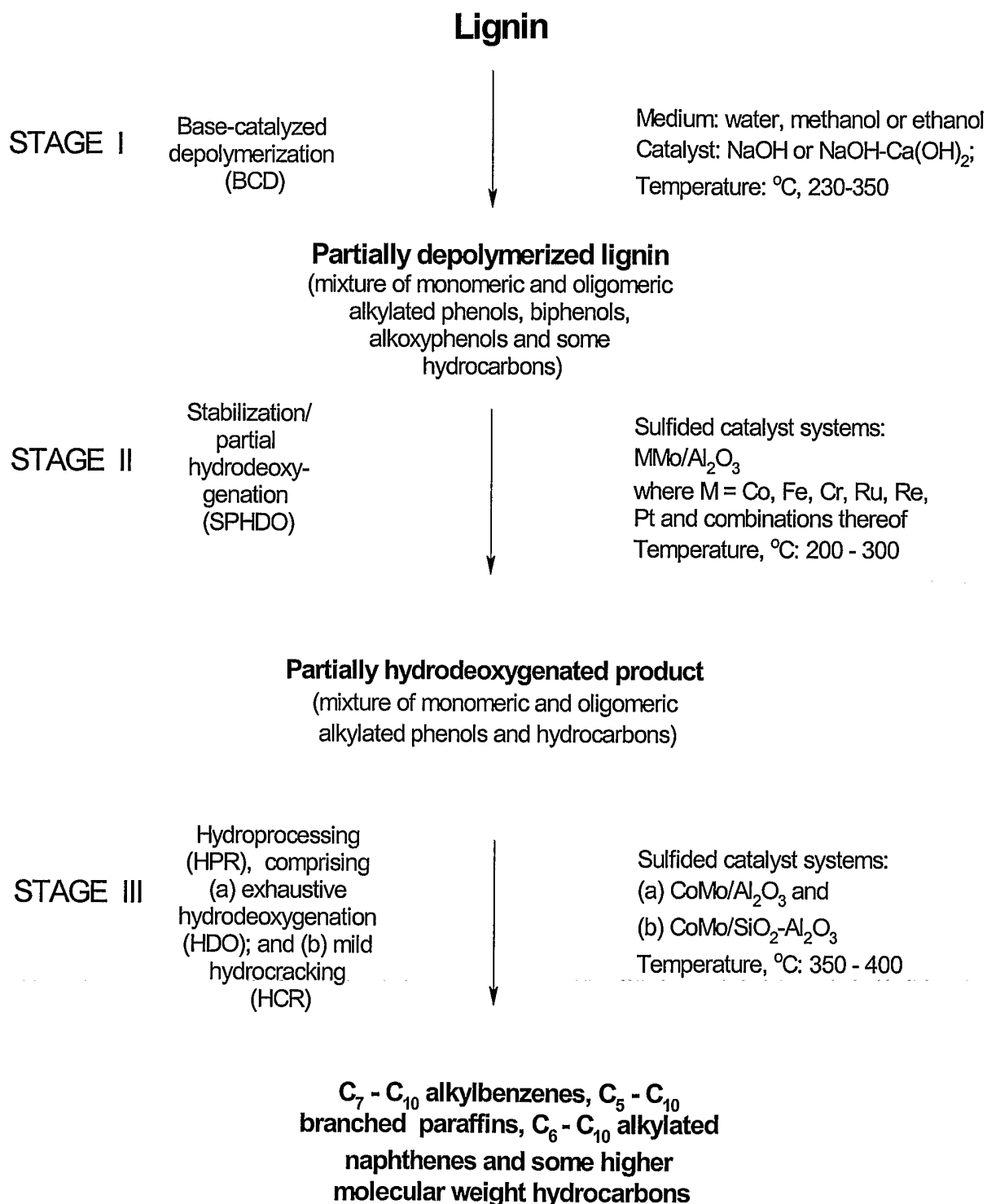


FIG. 1

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Lignin

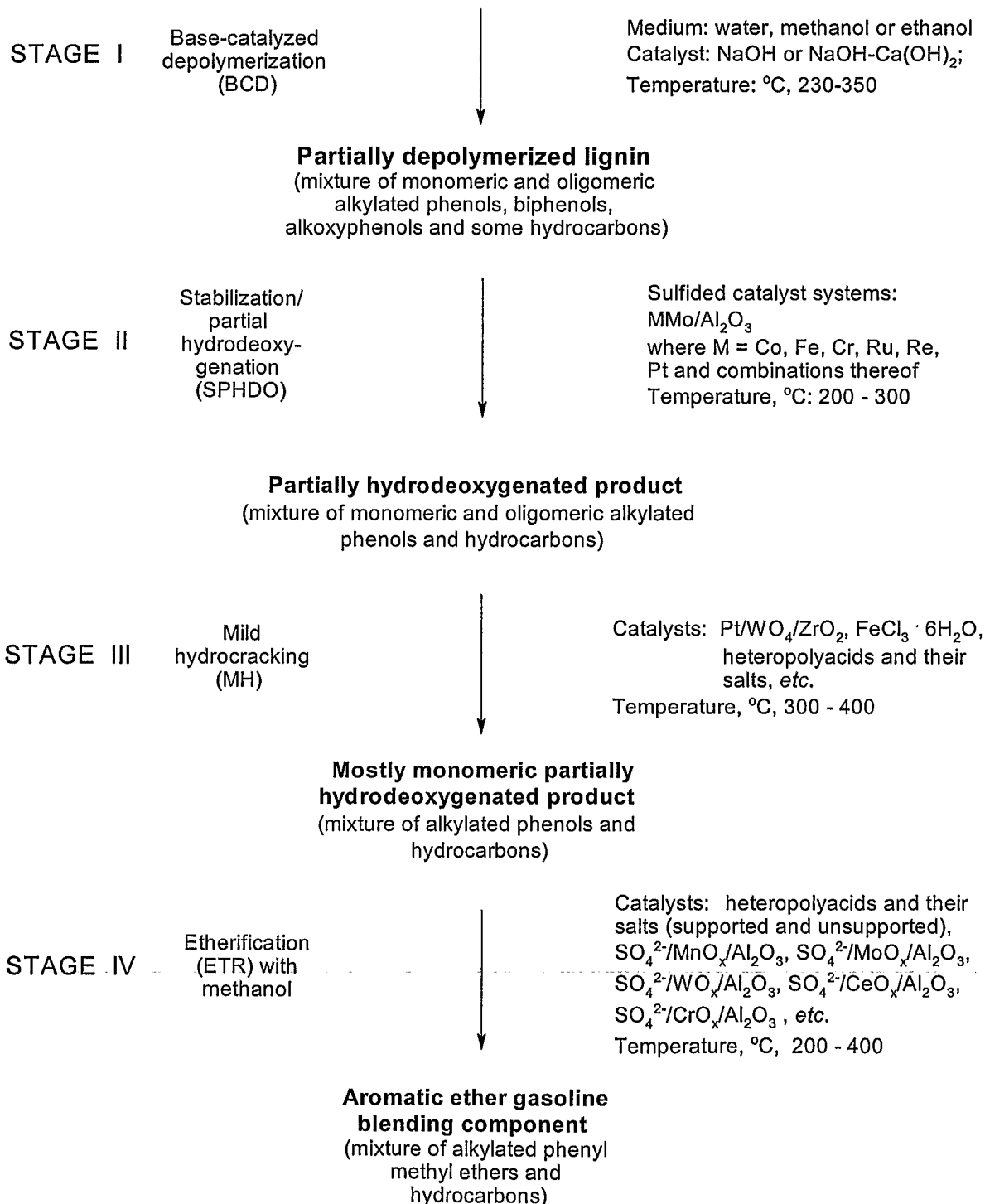


FIG. 2

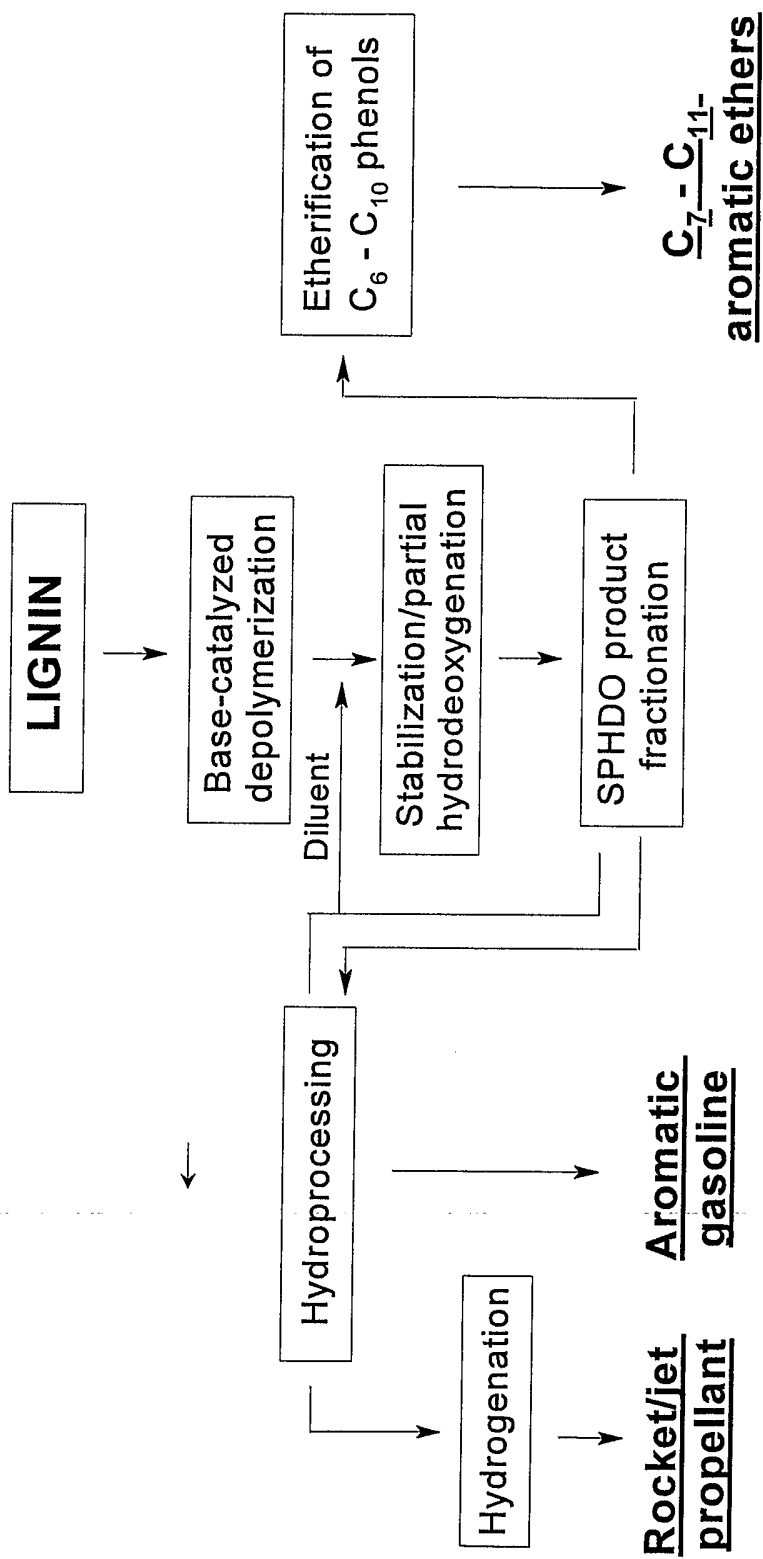


FIG. 3