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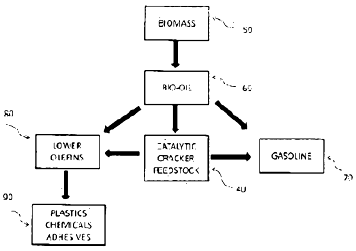

FIGURE 8A

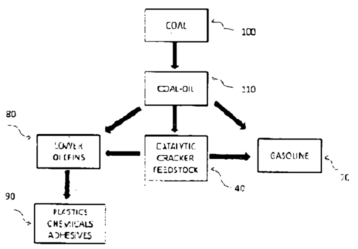

FIGURE 8B

(57) Abstract: The present invention relates to a method for producing a hydrocarbon product from coal and/or biomass comprising the following steps: converting the coal to a coal-oil and/or converting the biomass to bio-oil, optionally processing the coal-oil and/or bio-oil in a hydroprocessing reaction to remove one or more of oxygen, nitrogen or sulfur from hydrocarbon compounds in the coal-oil and/or bio-oil; and using at least a portion of the coal-oil and/or bio-oil as a feedstock in a cracking reaction to convert hydrocarbon compounds in the feedstock into a mixture of smaller hydrocarbon compounds comprising the hydrocarbon product.

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METHODS FOR PRODUCING HYDROCARBON PRODUCTS FROM BIO-OILS AND/OR COAL-OILS

INCORPORATION BY CROSS-REFERENCE

This application claims priority from NZ provisional application no. 580653 filed on 27 October 2009 and NZ provisional application no. 580654 filed on 27 October 2009, each of which is incorporated herein by cross-reference in its entirety.

FIELD OF THE INVENTION

The present invention relates generally to the production of hydrocarbon fuels and in particular the production of renewable hydrocarbon fuels. More specifically, the present invention provides processes for converting bio-oils produced from biomass and/or coal-oils produced from coals into hydrocarbon products such as gasoline and lower olefins.

BACKGROUND

Current processes for producing hydrocarbon products such as gasoline and lower olefins are generally conducted in conventional oil refineries and petrochemical complexes and rely on the distillation of crude oil.

Gasoline comprises aliphatic hydrocarbons with seven to eleven carbon atoms and is a petroleum product that is vital to the industrialised world. Gasoline is currently produced from crude oil in oil refineries, however, as world crude oil reserves are being rapidly depleted there are concerns regarding potential global shortages of gasoline in the future. Reduced crude oil supply is likely to lead to further increases in the price of gasoline. Furthermore, sulfur and nitrogen-containing compounds in crude oil have adverse affects on the environment during the production of gasoline and other hydrocarbon compounds such as lower olefins.

Lower olefins such as ethylene, propylene and butylene are hydrocarbon compounds used in the production of a large range of polymers (e.g. polyethyene, polypropylene, epoxy, polystyrene, and polychloroethene) and a variety of chemicals including ethylene oxide and acrolein. Polymers generated from lower olefins are used in the manufacture of products such as plastic bags, bottles, buckets, crates, ropes, carpets, insulation material and adhesives. Acrolein is used to produce glycerine, methionine, glutaraldehyde, and other organic chemicals. The current market value of lower olefins is relatively high due to the depletion of accessible fossil fuel supplies and is also expected to rise as the depletion of world crude oil reserves continues.

There is a need for alternative methods to produce hydrocarbon products such as gasoline and lower olefins that place less reliance on utilizing the depleting world reserves of crude oil. In particular, a need exists for alternative methods for producing hydrocarbon products from renewable sources. Preferably, the alternative methods have reduced adverse effects on the environment and/or provide hydrocarbon products of comparable or increased quality compared to methods utilising crude oil. Preferably, the alternative methods provide hydrocarbon products for reduced economic cost.

SUMMARY OF THE INVENTION

The present invention provides methods for producing hydrocarbon products such as gasoline and lower olefins from renewable sources. The methods of the present invention may have reduced adverse environment effects and/or economic cost compared to existing technologies relying on the extraction and use of crude oil. Additionally or alternatively, hydrocarbon products produced by the methods of the present invention may be of comparable or increased quality to those produced from crude oil and other similar feedstocks.

In one aspect the invention provides a method for producing a hydrocarbon product from coal comprising the following steps:

converting the coal to a coal-oil by thermal or hydrothermal conversion;

processing the coal-oil in a hydroprocessing reaction to remove one or more of oxygen, nitrogen or sulfur from hydrocarbon compounds in the coal-oil; and

using at least a portion of the coal-oil as a feedstock in a cracking reaction to convert hydrocarbon compounds in the feedstock into a mixture of smaller hydrocarbon compounds comprising the hydrocarbon product.

Also described herein is a method for producing a hydrocarbon product from coal comprising the following steps:

converting the coal to a coal-oil;

optionally processing the coal-oil in a hydroprocessing reaction to remove one or more of oxygen, nitrogen or sulfur from hydrocarbon compounds in the coal-oil; and

using at least a portion of the bio-oil as a feedstock in a cracking reaction to convert hydrocarbon compounds in the feedstock into a mixture of smaller hydrocarbon compounds comprising the hydrocarbon product.

In another aspect the invention provides a method for producing a hydrocarbon product from biomass comprising the following steps:

converting the biomass to bio-oil by thermal or hydrothermal conversion;

processing the bio-oil in a hydroprocessing reaction to remove one or more of oxygen, nitrogen or sulfur from hydrocarbon compounds in the bio-oil; and

using at least a portion of the bio-oil as a feedstock in a cracking reaction to convert hydrocarbon compounds in the feedstock into a mixture of smaller hydrocarbon compounds comprising the hydrocarbon product.

Also described herein is a method for producing a hydrocarbon product from biomass comprising the following steps:

converting the biomass to bio-oil;

optionally processing the bio-oil in a hydroprocessing reaction to remove one or more of oxygen, nitrogen or sulfur from hydrocarbon compounds in the bio-oil; and

using at least a portion of the bio-oil as a feedstock in a cracking reaction to convert hydrocarbon compounds in the feedstock into a mixture of smaller hydrocarbon compounds comprising the hydrocarbon product.

In another aspect the invention provides a method for producing a hydrocarbon product from a bio-oil, coal-oil, or mixture thereof, the method comprising:

optionally processing the bio-oil, coal-oil, or mixture thereof in a hydroprocessing reaction to remove one or more of oxygen, nitrogen or sulfur from hydrocarbon compounds in the bio-oil; and

using at least a portion of the bio-oil, coal-oil, or mixture thereof as a feedstock in a cracking reaction to convert hydrocarbon compounds in the feedstock into a mixture of smaller hydrocarbon compounds comprising the hydrocarbon product.

In one embodiment, the feedstock is comprised of at least 50% of the bio-oil and the hydrocarbon product is at least a 50% renewable product.

In another embodiment, the feedstock is comprised of at least 75% of the bio-oil and the hydrocarbon product is at least a 75% renewable product.

In one embodiment, the feedstock is comprised of at least 90% of the bio-oil and the hydrocarbon product is at least a 90% renewable product.

In one embodiment, the feedstock is comprised of at least 95% of the bio-oil and the hydrocarbon product is at least a 95% renewable product.

In one embodiment, the feedstock is comprised of at least 98% of the bio-oil and the hydrocarbon product is at least a 98% renewable product.

In one embodiment, the feedstock is 100% bio-oil and the hydrocarbon product is a 100% renewable product.

In one embodiment, the converting is by fast pyrolysis reaction.

In one embodiment, the hydroprocessing reaction includes a hydrodeoxygenation reaction.

In a particular embodiment the cracking reaction is a catalytic cracking reaction utilizing a powdered catalyst at a reaction temperature of between about 500°C and 600°C, and a reaction pressure of between about 1400 KPa and 2000 KPa.

In a further embodiment the cracking reaction is a catalytic cracking reaction utilized to convert hydrocarbons of C_{12} or above into a hydrocarbon product selected from any one or more of gasoline and fuel oil.

In a further embodiment the method comprises the step of processing the oil in a hydroprocessing reaction, wherein the hydroprocessing reaction additionally produces a hydrocarbon product selected from any one or more of a gasoline, lower olefins, and naphtha. Preferably the gasoline is of a high quality with a high octane number.

In another embodiment the step of processing the oil in a hydroprocessing reaction is omitted.

In one embodiment the method comprises the step of processing the oil in a hydroprocessing reaction, wherein the hydroprocessing reaction produces a naphtha intermediate.

In a further embodiment the cracking reaction is a steam cracking reaction utilizing steam at a reaction temperature of between about 850°C and about 1200°C to convert the naphtha into a hydrocarbon product selected from any one or more of fuel oil, gasoline, methane, ethane, LPG, and lower olefins.

In an additional embodiment the lower olefins are selected from any one or more of ethylene, propylene, butylenes, and combinations thereof.

In another embodiment the lower olefin is ethylene, propylene, butylene, butadiene, isoprene and other similar olefin compounds or combinations thereof.

In a further embodiment the method comprises the additional step of catalytically polymerizing the lower olefins, wherein the polymerizing produces a product selected from any one or more of plastic, polyethylene, polypropylene, synthetic rubber and adhesives.

In a further embodiment the method comprises the additional step of catalytically polymerizing the lower olefins, wherein the polymerizing produces a product selected from epoxy, polystyrene, and polychloroethene (PVC).

In another embodiment the method comprises additional step of oxidizing the lower olefins, wherein the oxidising produces an organic chemical product selected from any one or more of ethylene oxide and acrolein.

In another embodiment the method comprises additional step of oxidizing the lower olefins, wherein the oxidising produces an organic chemical product selected from any one or more of glycerine, methionine and glutaraldehyde.

In one embodiment the hydroprocessing reaction is a catalytic hydroprocessing reaction utilising a catalyst comprising an active metal or a combination of active metals.

In one embodiment the catalyst comprises at least one group VIB metal, at least one metal group VIII metal, or a combination thereof.

In one embodiment the catalyst is at least one of a cobalt-molybdenum (CoMo), nickel-molybdenum (NiMo) or nickel-tungsten (NiW) type catalyst.

In a particular embodiment the hydroprocessing reaction is performed in a hydroprocessing plant and produces C_1-C_4 hydrocarbons, and wherein said C_1-C_4 hydrocarbons are used as a fuel source for burners in said hydroprocessing plant.

In one embodiment the hydroprocessing reaction is performed in a single stage hydroprocessing plant or two-stage hydroprocessing plant.

In another embodiment the hydroprocessing reaction is performed in a multi-bed hydroprocessing plant or a series flow hydroprocessing plant.

In a further embodiment the hydroprocessing plant is integrated with a methanol plant, hydrogen produced from methanol plant is fed to the hydroprocessing plant for use in the catalytic hydroprocessing reaction, and C_1 to C_4 hydrocarbons produced from the hydroprocessing reaction are used as a feedstock for the methanol plant.

In another aspect the invention provides a hydrocarbon product produced by a method of the invention.

Other aspects, features and advantages of this invention will become apparent from the following detailed description when taken in conjunction with the accompanying drawings, which are a part of this disclosure and which illustrate, by way of example, principles of this invention.

BRIEF DESCRIPTION OF THE DRAWINGS

The following figures are used to illustrate the preferred embodiments of the invention and in no way are to be considered limiting.

Figure 1 shows a schematic of a single stage hydroprocessing plant according to an embodiment of the invention.

Figure 2 shows a schematic of a series flow oil hydroprocessing plant according to an embodiment of the invention.

Figure 3 shows a schematic of a two-stage hydroprocessing plant according to an embodiment of the invention.

Figure 4 shows a schematic of a methanol plant integrated with a hydroprocessing plant according to an embodiment of the invention.

Figure 5 shows a schematic of a steam reformer process for producing lower olefins and gasoline from naphtha according to an embodiment of the invention.

Figure 6 shows a schematic of a catalytic cracker according to an embodiment of the invention.

Figures 7a and 7b show flow charts representative of processes according to embodiments of the invention.

Figure 8a and 8b show flow charts representative of processes according to embodiments of the invention.

Figure 9 shows a schematic of a Micro Activity Test (MAT) unit comprising a fixed bed of catalyst contained in a Pyrex glass reactor supported in a temperature controlled furnace.

Figure 10 shows an H^1 NMR spectrum of lignite syncrude.

Figure 11 shows an H^1 NMR spectrum of bio-oil syncrude.

Figure 12 is a graph showing conversion (wt%) of lignite and bio-oil syncrude mixtures to all products which include gasoline, LCO, gas and coke.

Figure 13 is a graph showing product yields (wt%) of gasoline, light cycle oil (LCO), gases and coke from lignite and bio-oil syncrude mixtures.

Figure 14 is a graph showing gas yields (wt%) of propylene/TC3, butene/TC4, C1 and C2 carbons, and isobutene/isobutane from lignite and bio-oil syncrude mixtures.

DEFINITIONS

As used herein, the singular forms "a", "an" and "the" include plural references unless the context clearly dictates otherwise. For example, reference to "a hydroprocessing reaction" also includes a plurality of hydroprocessing reactions.

As used herein, the term "lower olefin", also known as alkenes, is to be understood to refer to any unsaturated hydrocarbon comprising one or more carbon to carbon double bond and having two, three, four or five carbon atoms. Non-limiting examples of lower olefins include cyclic or acyclic olefins, monoolefins, diolefins, triolefins, ethylene, propylene, butylene, butadiene and isoprene.

As used herein, the word "coal" is to be understood to refer to any form of coal that may be used to produce coal oil. Non-limiting examples of coal include anthracite, bituminous, sub-bituminous, and lignite.

As used herein, the term "coal oil " is to be understood to refer to any oil product derived partially or wholly from the treatment of coal (e.g. by pyrolysis or any other means).

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

As used herein, the term "oil hydroprocessing plant" will be understood encompass any hydroprocessing plant capable of refining oil, including for example, bio-oil, coal-oil, crude oil, and any combination thereof.

As used herein, the term "hydrocarbon product" it to be understood to refer to a hydrocarbon compound that has been subjected to hydroprocessing reaction(s) and/or cracking reaction(s).

As used herein, the word "gasoline" will be understood to refer to a hydrocarbon product comprising saturated and/or unsaturated hydrocarbons of about C_3 to about C_{12}, and more preferably comprising saturated and/or unsaturated hydrocarbons of about C_4 to about C_{10}.

As used herein, the term "bio oil" will be understood to be a reference to any mixture of liquid organic materials obtained by conversion of biomass (e.g. by thermal, hydrothermal and/or catalytic conversion or by any other means).

It will be understood that use of the word "about" herein in reference to a recited numerical value includes the recited numerical value and numerical values within plus or minus ten percent of the recited value.

It will be understood that use of the word "between" herein when referring to a range of numerical values encompasses the numerical values at each endpoint of the range. For example, a temperature range of between 10°C and 15°C is inclusive of the temperatures 10°C and 15°C.

As used herein, the word "comprising" is to be understood in its "open" sense, that is, in the sense of "including", and thus not limited to its "closed" sense, that is the sense of "consisting only of". A corresponding meaning is to be attributed to variations of the words "comprising" such as "comprise", "comprised" and "comprises". Thus, for example, a method "comprising" two steps may consist exclusively of those two steps or may include one or more additional steps.

DETAILED DESCRIPTION

A need exists for alternative methods to produce hydrocarbon products such as gasoline and lower olefins. As crude oil becomes scarcer and more costly the need for alternative means of producing fuels and lower olefins from non-crude oil feedstocks (e.g. biomass and lignite) increases. The methods described herein enable biomass to be converted into gasoline and lower olefins based on renewable feedstocks and thus meet this need.

The present invention provides methods for producing hydrocarbon products which may have reduced adverse effects on the environment and/or provide hydrocarbon products of comparable or increased quality compared to existing processes that rely on the use of crude oil. The methods of the present invention may also provide hydrocarbon products for reduced economic cost in comparison to existing processes that rely on the use of crude oil.

Oil Production

Bio-oil

Economic and/or environmental advantages may be derived from producing hydrocarbon products such as gasoline and lower olefins from bio-oil that is produced from renewable biomass sources. Certain aspects of the present invention provide methods for producing such hydrocarbon products from various sources of biomass.

The biomass can be derived from any suitable source. For example, a variety of animal and plant sources such as plants, trees, forestry waste, corn waste, algae, crops, landfill gas, garbage, palm oil and other vegetable oils. Waste products from animal processing such as tallow may also be considered as renewable sources of biomass suitable for use in the methods of the present invention.

Bio-oil can be produced from biomass using any suitable method known in the art.

For example, a fast pyrolysis reaction may be used to convert biomass into bio-oil. The fast pyrolysis reaction may comprise heating the biomass material in an oxygenated or reducing atmosphere, sometimes with steam, for a short time (e.g. several seconds). This reaction may break down the biomass into a large number of relatively small molecules. The mixture may then be quickly cooled to prevent further reaction and produces the dark oily liquid called bio-oil. A non-limiting example of a fast pyrolysis process is described in U.S. patent no, 4,485,003, the contents of which are incorporated herein by cross-reference in their entirety.

Additionally or alternatively, bio-oil can also be produced from biomass by a thermochemical reaction. The thermochemical reaction may comprise heating the biomass material in supercritical solvent (e.g, supercritical water) for a suitable period of time (e.g. several minutes). The thermochemical reaction may result in the hydrolysis of biomass leading to a light stable bio-oil. A non-limiting example of a suitable thermochemical reaction method is described in International PCT publication no. WO2009/015409 and corresponding United States patent application no. 12/670838, the contents of each of which are incorporated herein by cross-reference in their entirety.

Additionally, or alternatively bio-oil may be produced from biomass using the method as described in United States patent no. 6,180,845, the contents of which are incorporated herein by cross-reference in their entirety.

Coal-oil

Economic and/or environmental advantages may be derived from producing hydrocarbon products such as gasoline and lower olefins from coal-oil produced from coal. Certain aspects of the present invention provide methods for producing such hydrocarbon products from various sources of coal.

The coal may be derived from any suitable source. For example, there are considerable reserves of coal and in particular brown coal (lignite) available globally which may potentially provide an oil suitable for use in the methods of the invention.

Coal-oil can be produced from coal using any suitable method known in the art.

A suitable coal to coal-oil conversion process includes liquefaction of coal by hydrogenation as described, for example, in U.S. patent 4,243,509 (the contents of which are incorporated herein by cross-reference in their entirety).

Additionally or alternatively, thermochemical conversion of coal to coal-oil may be utilized as described in International PCT publication no. WO2009/015409 and corresponding United States patent application no. 12/670838, U.S. patent no. 3,850,738, or U.S. patent no. 4,485,003, the contents of each of which are incorporated herein by cross-reference in their entirety.

Blended Oil

In certain embodiments of the invention a blended oil may be utilized. In general, at least a portion of the blended oil is made up of bio-oil and/or coal-oil. The blended oil may further comprise crude oil and/or oil derived from alternative feedstocks such as plant oils, algae oils, or oils from other alternative feedstock sources.

For example, the blended oil may comprise at least about 5%, 10%, 15%, 20%, 25%, 30%, 35%, 40%, 45%, 50%, 55%, 60%, 65%, 70%, 75%, 80%, 85%, 90% or 95% bio-oil.

For example, the blended oil may comprise at least about 5%, 10%, 15%, 20%, 25%, 30%, 35%, 40%, 45%, 50%, 55%, 60%, 65%, 70%, 75%, 80%, 85%, 90% or 95% coal-oil.

In some embodiments, a bio-oil may be comprised of a mixture of bio-oil together with fossil oil (e.g. crude oil) and/or coal-oil and/or a gas condensate.

In other embodiments, a coal-oil may be comprised of a mixture of coal-oil together with another fossil oil (e.g. crude oil), bio-oil, and/or a gas condensate.

Hydroprocessing reactions

In accordance with the methods of the present invention, an oil (e.g. bio-oil, coal-oil or blended oil) may be hydroprocessed to remove or reduce any one or more of oxygen, nitrogen and sulfur, and/or hydrogenate aromatic structures in the oil. Performing the hydroprocessing step may increase the quality of the oil for use as a feedstock in subsequent cracking reactions, resulting in a higher yield of gasoline and/or lower coke production. For example, the oxygen content of bio-oil and coal-oil may be relatively high (e.g. 40%) and the removal of oxygen from hydrocarbon structures by performing a hydroprocessing step may increase the quality of the oil for use as a feedstock in subsequent cracking reactions.

In certain embodiments of the invention, the hydroprocessing step is optional and may not be required. This may the case, for example, where a bio-oil of low oxygen and/or low nitrogen and/or low sulfur content is generated. For example, a bio-oil having an oxygen content of less than about 15%, preferably less than about 10%, more preferably less than about 5% and still more preferably less than about 2% may be subjected to cracking reactions (e.g. catalytic cracking) in accordance with the methods described herein without a preceding hydroprocessing step. The bio-oil may have a sulfur content of less than about 200ppm, preferably less than about 100ppm, more preferably less than about 50ppm, and still more preferably less than about 10ppm. The bio-oil may have a nitrogen content of less than about 200ppm, preferably less than about 100ppm, more preferably less than about 50ppm ,and still more preferably less than about 10ppm.

A primary hydroprocessing step that may be used for a bio-oil or coal-oil feedstock may be a catalytic hydrodeoxygenation step to remove the oxygen from the hydrocarbon structures. Additional hydrodenitrogenation step and/or desulphurisation steps may be included to remove any nitrogen and/or sulphur present in the oil. In addition, aromatic hydrocarbon structures also exist in bio-oil/coal-oil feedstocks. These aromatic hydrocarbon structures may benefit from being hydrogenated to improve suitability for use in subsequent cracking reactions. This may consequently improve the quality of gasoline and/or lower olefin hydrocarbon products obtained by methods of the present invention. Furthermore, in the case where oxygen concentration in the bio-oil or coal-oil is high, the consumption of hydrogen in the hydrodeoxygenation step may be substantial.

The following is an example of a hydrodeoxygenation reaction:

$C_nO_nH_{2n} + (n+1)H_2 \rightarrow nH_2O + C_nH_{(2n+2)}$

The hydrogen required for hydroprocessing reactions, and in particularly the hydrodeoxygenation step, may be derived from any source. For example, the hydrogen may be sourced from a steam reformer and/or excess hydrogen produced in a by-product stream of a methanol plant as described in International PCT application no. PCT/NZ/2010/000105.

Additionally or alternatively, the hydrogen may be sourced from the steam reformer from a methanol plant or from other known hydrogen sources such as a catalytic reformer or a combination of any of these sources.

In further embodiments of the invention, a bio-oil, coal-oil and/or blended oil of the invention may be mixed together with a paraffinic feedstock such as a gas condensate to reduce the rate of hydrodeoxygenation and thereby avoid rapid catalyst deactivation in the hydroprocessing step (see, for example, International PCT application no. PCT/NZ/2010/000105, the contents of which are incorporated herein by cross-reference in their entirety).

The utilization of, for example, a highly paraffinic gas condensate may reduce the overall hydrogen requirement in the hydroprocessing reactions. A high concentration of oxygen-containing molecules in the bio-oil and/or coal oil may increase the rate of the hydrodeoxygenation reactions in the hydroprocessing reactors and may cause coke formation on the catalyst. The inclusion of a highly paraffinic gas condensate may dilute the concentration of the oxygen-containing molecules in the bio-oil and/or coal oil and may enhance the rate of the hydrodeoxygenation reactions. The highly paraffinic gas condensate may assist in reducing the rate of catalyst deactivation by setting up a hydrogen-equilibrium on the surface of the catalysts which assists in preserving the life of the catalysts. Furthermore, diluting the concentration of oxygen-containing molecules in the bio-oil and/or coal oil with gas condensate may improve the heat distribution from the exothermic hydrodeoxygenation reactions over a reactor in which the reactions are performed and may reduce the amount of coke formation on the catalyst, thus further improving the life of the catalyst.

In another embodiment, a detergent may also be added to the bio-oil and/or coal oil feedstock to facilitate the mixing of the hydrophilic bio-oil and/or coal oil with the gas condensate.

Hydroprocessing reactions in accordance with the methods of the present invention may be performed in an oil hydroprocessing plant. An oil hydroprocessing plant in accordance with the invention includes any known oil hydroprocessing plant configurations or combinations thereof. Suitable oil hydroprocessing plant configurations are described, for example, in "*Hydrocracking Science and Technology*", by Julius Scherzer and A.J. Gruia. Macell Dekker, (1996), p 13-71. Single stage or multi-bed oil hydroprocessing plants may be employed.

For example, the hydroprocessing plant may be a single stage hydroprocessing plant or a two-stage hydroprocessing plant. The hydroprocessing plant may comprise a single stage reactor bed or multiple reactor beds. The hydroprocessing plant may be a multi-bed hydroprocessing plant or a series flow hydroprocessing plant. The hydroprocessing plant may be a fixed bed reactor with down-flow of liquid and gas. The reactor may be packed with several beds in series with quenching of the mixture between the beds to control the temperature of the reactors as the hydroprocessing reactions may be highly exothermic. The reactor beds may be packed with appropriate catalysts to perform the hydroprocessing reactions.

It is to be understood that the term feedstock as used herein with respect to a hydroprocessing plant is defined as a feedstock including any one of a bio-oil feedstock produced from biomass, a coal oil feedstock produced from coal, a combination of bio-oil and coal oil feedstock and/or a combination of any one of these feedstocks with other hydrocarbon mixtures such as crude oil and/or a gas condensate.

Figure 1 shows a single stage reactor oil hydroprocessing plant 300 according to one exemplary embodiment of the invention. The feedstock 360 may be fed into the hydroprocessing plant and may be pre-mixed with hydrogen 340. The hydrogen 340 can optionally be compressed to the required reaction pressure in a makeup compressor 342 prior to use in the hydroprocessing reactions. The pressurized hydrogen 340 from the makeup compressor 342 may be fed to the hydroprocessing reactor 350 under pressure and mixed with the feedstock 360. Alternatively the hydrogen may be fed directly to the hydroprocessing reactor 350 (*not shown*).

The flow of hydrogen 340 into the hydroprocessing reactor 350 can be maintained above about 1 kg hydrogen/bbl feed (420 s.c.f./bbl) of feed and preferably in the range 2 to 20 kg hydrogen/bbl feed (840 to 8400 s.c.f./bbl.) More generally, at least sufficient hydrogen may be provided to supply that consumed in the conversion of the oxygen containing compounds present in the feedstock and to compensate for incidental hydrogenation of nitrogen and sulfur compounds, while maintaining a significant excess of hydrogen partial pressure. Hydrogen 340 can be added to the feed prior to introduction of the feed into the hydroprocessing reactor 350, and/or added separately to the hydroprocessing reactor 350. Excess hydrogen can be removed and recycled to the reaction zone.

The hydrogen 340 is preferably provided at a pressure of about 2×10^6 N/m^2 to about 20×10^6 N/m^2 (about 20 to 200 bar), and more preferably at a pressure of about 4×10^6 N/m^2 to 8×10^6 N/m^2 (about 40 to 80 bar). The feedstock can be preheated to the appropriate initial reaction temperature using the heater 352 before entering the hydroprocessing reactor 350.

The hydrodeoxygenation reactions in the hydroprocessing reactor 350 can typically be performed at a reaction temperature between about 200°C to about 500°C, and preferably between about 250°C and about 400°C. However, the skilled addressee will recognise that the particular temperature used in the reaction may vary depending upon the oil feedstock and/or particular catalyst(s) used in the reactions. The reactions can also be typically performed at pressures of from about 2×10^6 N/m^2 (20 bar) to about 20×10^6 N/m^2 (200 bar), and more preferably at a pressure of 4×10^6 N/m^2 (40 bar) to 12×10^6 N/m^2 (120 bar). For a fixed bed hydroprocessing reactor the weight hourly space velocity (WHSV) is typically in the range of 0.1 to 10 hr^{-1} and preferably 0.5 to 5.0 hr^{-1}. As for temperature the particular pressure or WHSV used in the reaction may vary depending on the particular feedstock and catalyst used in the reaction.

Catalyst(s) used in the hydroprocessing reactions may include any known hydroprocessing reaction catalysts. Preferred catalysts for the hydroprocessing reactions may be comprised of a combination of at least two active metals wherein at least one metal is from group VIB and/or at least one metal from group VIII of the periodic table of elements. The commonest combinations are of cobalt-molybdenum (CoMo), nickel-molybdenum (NiMo) and nickel-tungsten (NiW) type. Preferably each of the active metals is incorporated onto a metal oxide support, such as alumina, amorphous silica alumina and/or zeolites, such as zeolite Y, in an amount of from about 0.1 percent to about 20 percent by weight of the total catalyst. The alumina support of the catalyst is generally the gamma form thereof. In some cases, the alumina support could include up to 10% of silica. The single stage reactor configuration may contain a single catalyst or more than one catalyst in different catalyst beds, preferably the reactor contains a single catalyst. Any suitable catalyst or combination of different catalysts may be used in the hydroprocessing reactions. Preferred catalysts for the hydroprocessing reactions may be comprised of a combination of one or more (e.g. two) active metals wherein at least one metal is from group VIB and/or at least one metal from group VIII of the periodic table of elements. Suitable combinations include those comprising the cobalt-molybdenum (CoMo), nickel-molybdenum (NiMo) and nickel-tungsten (NiW) type/s. Combinations may also include monometallic catalysts (e.g. Co, Mo, W sulfides). Non-limiting examples of suitable catalysts include $Pt/Al_2O_3/SiO_2$, $Pd/Al_2O_3/SiO_2$, $Ni/Al_2O_3/SiO_2$, NiO/MoO_3, CoO/MoO_3, NiO/WO_2 and mixtures thereof.

Preferably each of the active metals is incorporated onto a metal oxide support, such as alumina, amorphous silica alumina and/or zeolites, such as zeolite Y, in an amount, for example, of from about 0.1 percent to about 20 percent by weight of the total catalyst.

The alumina support of the catalyst may be the gamma form thereof. In some cases, the alumina support may include silica (for example, up to 10% silica). The single stage reactor configuration may contain a single catalyst or more than one catalyst in different catalyst beds.

The single stage reactor may, for example, contain a catalyst at the top of the bed with a relatively low activity for hydrodeoxygenation. This may avoid or reduce rapid reaction rates leading to local hot spots and coking of the catalyst causing rapid deactivation. Low activity hydrodeoygenation catalysts may comprise, for example, a single metal such as Mo or W or combinations of metals such as Ni/Mo or Ni/W supported on gamma alumina, preferably with relatively low metal loadings in the range of 0.1-15%wt.

For series flow and two-stage hydroprocessing configurations different catalysts are typically deployed in each reactor stage although this is not a strict requirement. In certain embodiments, catalysts used in the single stage configuration or the first stage reactor of the series flow and two stage configurations may be based on an alumina support impregnated with cobalt-molybdenum (CoMo) or nickel-molybdenum (NiMo) as the active hydrogenation metals. In certain embodiments, catalysts used in the second stage reactor for series flow and two stage hydroprocessing configurations may be amorphous silica alumina and/or a zeolites, such as zeolite Y impregnated with cobalt-molybdenum (CoMo), nickel-molybdenum (NiMo) or nickel-tungsten (NiW) to provide both a hydrogenation function and a cracking function for the catalyst.

In addition, for series flow and two stage hydroprocessing configurations a first catalyst in the first reactor may contain a low activity hydrodeoxygenation catalyst to avoid rapid reaction rates and fast catalyst deactivation due to coke formation. The low activity hydrodeoygenation catalysts may comprise, for example, a single metal such as Mo or W or combinations of metals such as Ni/Mo or Ni/W supported on gamma alumina, preferably with relatively low metal loadings in the range of 0.1-15%wt.

Referring again to **Figure 1**, in certain embodiments the effluent mixture may be piped through heat exchangers to assist in preheating the feedstock 360 and cooling the effluent mixture (not shown). Wash water may also be mixed with the effluent mixture to assist in removing the impurities such as sulfur, nitrogen and oxygen, by converting the impurities to aqueous compounds. The effluent mixture may then be fed to a condenser 356 to condense the hydrocarbons in the effluent mixture. The condensed mixture may then be separated from the hydrogen gas present in the mixture in a separator 374. The hydrogen gas may be fed back as indicated by arrow 346 to the reactor and optionally to compressor 342 to increase the pressure of the hydrogen. The water soluble aqueous compounds containing the impurities may be removed as sour water.

The separated hydrocarbon mixture from the separator 374 may be fed to an appropriate apparatus to separate the different hydrocarbon components according to the number of carbon atoms such as, for example, distillation column 380. The lighter gas products 382, e.g. C_1-C_2, or C_1-C_4 may be piped back to the steam reformer of the methanol plant (not shown) or used as a fuel source for the burners in the oil hydroprocessing plant. The liquid hydrocarbon products such as naphtha 384 and diesel 388 may be collected for further refining into transportation fuels. The heavy hydrocarbon products 390 may be recycled back as input to the hydroprocessing reactor 350 through recycle pump 394 and then pipe 392.

The separated hydrocarbon mixture from the separator 374 may be fed to a distillation column 380 to separate the different hydrocarbon components according to the number of carbon atoms. The lighter gas products 382, e.g. C_1-C_2, or C_1-C_4 may be collected, optionally the lighter gas products 382, e.g. C_1-C_2, or C_1-C_4 may be piped back to a steam reformer of a methanol plant (not shown) or used as a fuel source for the burners in the hydroprocessing plant. The heavy oil hydrocarbon products 390 may be collected as the catalytic cracker feedstock. This catalytic cracker feedstock 390 may thus be based at least in part on bio-oil and/or coal oil.

In certain embodiments, liquid naphtha hydrocarbon 384 product may be collected and, for example, refined into lower olefins (e.g. in a steam cracker) in accordance with the methods of the invention.

In certain embodiments, gasoline and naphtha hydrocarbon products may be collected directly from the distillation column 380 of the hydroprocessing plant.

In some embodiments, heavy hydrocarbon products 390 may be recycled back as input to the hydroprocessing reactor 350 through recycle pump 394 and then pipe 392.

In other embodiments, heavy hydrocarbon products 390 may be collected and, for example, refined into gasoline and or lower olefin hydrocarbon products (e.g. in a catalytic cracker) in accordance with the methods of the invention.

Multi-bed hydroprocessing plants may be utilized to provide a higher level or complete conversion of feedstock into the desired hydrocarbon product(s). **Figure 2** shows a series flow hydroprocessing plant according to an exemplary embodiment of the invention. In the illustrated hydroprocessing plant configuration there is shown a first reactor 550 and a second reactor 551, although it is noted that there may be three, four, five, six or more reactors if desired. Each reactor 550, 551 may comprise the same or different catalyst beds. In a preferred arrangement the first reactor 550, or earlier reactors if more than two reactors, comprises catalysts bed(s) to adapted to remove oxygen and/or nitrogen and/or sulphur from oil feedstock 360. Thus the first reactor 550 is preferably designed to perform hydrodeoxygenation reactions and/or hydrodenitrogenation reactions and/or desulphurisation reactions. Non-limiting examples of catalysts that may be included in catalyst beds of the first reactor 550 (or the earlier reactors) include transition metal sulfides on an appropriate support such as gamma-alumina or zeolite (e.g. sulfided CoMo and NiMo catalysts supported on γ-Al_2O_3).

To avoid rapid catalyst deactivation due to coking the first catalyst bed or beds in the first reactor may contain a relatively low activity hydrodexygenation catalyst. The low activity hydrodeoygenation catalysts may comprise, for example, a single metal such as Mo or W, or combinations of metals such as Ni/Mo or Ni/W supported on gamma alumina, preferably with relatively low metal loadings in the range of 0.1-15%wt. In the case of series flow and two stage reactors the first reactor may preferably contain catalyst with the composition of Ni/Mo supported on gamma alumina and the second stage catalyst may preferably contain Ni/W supported on gamma alumina or amorphous silica alumina and/or a zeolite, such as zeolite Y impregnated with cobalt-molybdenum (CoMo), nickel-molybdenum (NiMo) or nickel-tungsten (NiW), to provide both a hydrogenation function and a cracking function for the catalyst.

The second or later reactors 551 may comprise catalyst beds adapted to break up the hydrocarbons present in the feedstock 360 by hydrocracking. In this hydroprocessing plant configuration the feedstock 360 and hydrogen 340 may be initially feed via heater 352 into the first reactor 550 and then subsequently fed into the second reactor 551. This series configuration may provide improved control of catalytic reactions and can spread the hydroprocessing reactions over more than one reactor. As for the single stage hydroprocessing reactor described in relation to **Figure 1** above the effluent mixture from the reactors may be processing through one or more separators such as a hot separator 574, high pressure separator 374 and/or low pressure separator 674. A number of heat exchanges 596 may be used to recycle the heat produced in the exothermic reactions. The separated hydrocarbon mixture from the separators 374, 574, 674 is fed to a distillation column 380 to separate the different hydrocarbon components according to the number of carbon atoms. The lighter gas products 382, e.g. C_1-C_2, or C_1-C_4 may optionally be piped back to a steam reformer of a methanol plant (not shown) or used as fuel for burners or collected for other uses. Liquid hydrocarbon products such as naphtha 384 and diesel 388 may be collected for further refining into transportation fuels. The heavy hydrocarbon products may be recycled back as an input to the hydroprocessing reactor 550 through recycle pipe 392.

Figure 3 shows a two stage flow hydroprocessing plant according to an exemplary embodiment of the invention. In the illustrated hydroprocessing plant there is first reactor 650 and a second reactor 651, each reactor comprising different catalyst beds. In a preferred arrangement the first reactor 650 comprises catalysts beds adapted to perform dehydrogenation reactions to remove oxygen and/or nitrogen and/or sulphur from the feedstock 360. Thus, the first reactor 650 may be preferably designed to perform hydrodeoxygenation reactions and/or hydrodenitrogenation reactions and optionally some desulphurisation reactions if required, although some hydrocracking reactions may also occur in the first reactor 650. The second or later reactors 651 may comprise catalyst beds adapted to crack the hydrocarbons present in the feedstock 360 by performing hydrocracking reactions. The second reactor 651 generally comprises acidic catalysts also with hydrogenation activity. The second reactor 651 may comprise strongly acidic catalysts to perform the hydrocracking reactions. In the illustrated two stage hydroprocessing plant configuration the oil feedstock 360 and hydrogen 340 are initially feed via heater 352 into the first reactor 650, the hydrogen 340 passing through heater 352. Effluent mixture from the first reactor 650 may be cooled at condenser 656 and then separated in one or more separators such as high pressure separator 374 and low pressure separator 674 and fed to the distillation column 380 to remove the produced hydrocarbon products, such as naphtha 384 and diesel 388. The remaining heavy hydrocarbon products 390 may be recycled to the second reactor 651 where the majority of the hydrocracking reactions may occur. The heat produced in these exothermic reactions may be recycled using a number of heat exchanges 696 to assist in controlling the temperature of the reactions. The effluent mixture produced from the second reactor 651 may be mixed with the effluent from the first reactor 650 and again cooled at condenser 656 and then separated in one or more separators such as high pressure separator 374 and low pressure separator 674 and fed to the distillation column 380 to remove the produced hydrocarbon products, such as naphtha 384 and diesel 388. The remaining heavy hydrocarbon products 390 may again be recycled to the second reactor 651 for further processing. This two-stage configuration may provide a more complete conversion of the oil feedstock into the desired hydrocarbon products (e.g. naphtha) due to the repeated recycling of the heavy products back to the second reactor 651.

For series flow and two-stage hydroprocessing different catalysts may be deployed in each reactor stage. Typically, catalysts used in the single stage configuration or the first stage reactor of the series flow and two stage configurations will based on an alumina support impregnated with cobalt-molybdenum (CoMo) or nickel-molybdenum (NiMo) as the active hydrogenation metals. For the second stage reactor for the series flow and two stage configurations, amorphous silica alumina and/or a zeolites, such as zeolite Y, will normally be deployed impregnated with cobalt-molybdenum (CoMo), nickel-molybdenum (NiMo) or nickel-tungsten (NiW) or noble metal catalysts such as platinum (Pt) and palladium (Pd) or combinations thereof to provide both a hydrogenation function and a cracking function for the catalyst.

In a further embodiment any one of the hydroprocessing plant configurations described above may be combined and integrated with a chemical processing methanol plant to feed co-products produced in the methanol plant as an input to the hydroprocessing plant. Suitable integrated plants are described, for example, in International PCT application no. PCT/NZ2010/000105, the entire contents of which are incorporated herein by reference in their entirety. Furthermore, co-products from the hydroprocessing plant can be used as an additional feedstock into the methanol plant. The integration of the methanol plant with a hydroprocessing plant allows utilization of the excess hydrogen waste stream produced in the methanol plant, or hydrogen produced from a steam reformer from a methanol plant, to be used as a hydrogen source for the bio-oil and/or coal oil hydroprocessing plant providing significant cost savings in sourcing hydrogen, reducing the requirement of an additional catalytic reformer for the hydroprocessing plant to provide the required hydrogen. This may reduce the emission of GHG such as carbon dioxide (CO_2) that are released from catalytic reformers utilized to produce hydrogen in a traditional hydroprocessing plant.

Optionally the light gaseous hydrocarbon products, such as C_{1-4} hydrocarbon products, produced in the hydroprocessing plant are piped back to the methanol plant and used as an additional feedstock. When bio-oil is used in the feedstock for the oil hydroprocessing reactions, the level of non-renewable natural gas feedstock used in the methanol plant may be reduced resulting in a decrease in the environmental impact of producing methanol. Furthermore, methanol produced in an integrated processing plant may be produced in part from a renewable feedstock when the feedstock comprises bio-oil, resulting in a renewable methanol. The higher the percentage of bio-oil used in the feedstock for a bio-oil hydroprocessing plant the more renewable products are produced and are consequently available for utilization as an alternative feedstock to the methanol processing plant. Thus, producing methanol from a higher level of renewable feedstock source and reducing the level of non-renewable natural gas required, resulting in a higher level of renewable methanol. This reduction in the use of non-renewable natural gas significantly reduces the environmental impact of producing methanol.

Figure 4 shows an outline of an integrated plant 210 showing integration of a hydroprocessing plant with a methanol plant according to an exemplary embodiment of the invention. In the illustrated embodiment, the integrated plant 210 facilitates the use of the hydrogen co-product produced from the methanol plant 230 in a hydroprocessing plant 250. The integrated plant 210 comprises a hydrocarbon feedstock 212 which may be feed to a steam reformer 220 together with steam 214 to produce synthesis gas 228. The synthesis gas 228 may then be fed to the methanol plant 230 which includes a methanol reactor (not shown). The crude methanol 236 produced from the methanol plant 230 may be separated and processed for further purification 238 and the gaseous stream by-product containing hydrogen 240 may be piped to the hydroprocessing plant 250 as an input to the hydroprocessing reaction. The utilization of the hydrogen from the methanol plant or steam reformer from a methanol plant to the hydroprocessing plant may provide significant cost savings in obtaining the required hydrogen for the hydroprocessing reactions.

In the hydroprocessing plant 250 a bio-oil and/or coal oil containing feedstock 260 may be mixed with the hydrogen 240 from the methanol plant 230 in a hydroprocessing reactor in the presence of catalyst(s) as described above. The hydroprocessing reaction can be performed under appropriate reaction conditions in the hydroprocessing reactor 250 as outlined above. The hydrocarbon products 270 produced can then be separated into the different product groups for example using a distillation column 280. In a preferred embodiment the light gaseous such as C_{1-2} or C_{1-4} hydrocarbon products 282 may be recycled back, via a pipe, as a supplementary feedstock to the steam reformer reactor 220 as indicated by arrow 284. Additionally or alternatively, as in a traditional hydroprocessing plant, the liquid petroleum gas (LPG) component of the light gaseous hydrocarbon products, C_3-C_4, may be extracted and the remaining light gaseous hydrocarbon products, C_1-C_2, used as a fuel for the burners and heaters in the integrated processing plant (not shown). The heavy hydrocarbon products 290, for example C_{17} products or greater, may be optionally recycled back as a feed to the hydroprocessing reactor 250 as indicated by arrow 292, or used as a feedstock to a catalytic cracker. The hydrocarbon products C_{5-20}, preferably C_{5-16} such as naphtha 286, can be collected as a feedstock for producing lower olefins, for example, by use as a feedstock for a steam cracker process as described in more detail below.

Cracking reactions

In accordance with the methods described herein, cracking reactions may be utilized to produce one or more desired hydrocarbon products from an oil of the invention (e.g. bio-oil, coal-oil or blended oil) or a derivative of an oil of the invention that has undergone hydroprocessing.

In certain embodiments, an oil of the invention (e.g. bio-oil, coal-oil or blended oil) may be subjected to catalytic cracking reactions to produce one or more desired hydrocarbon products without a performing a preceding hydroprocessing step.

In other embodiments, an oil of the invention (e.g. bio-oil, coal-oil or blended oil) may be subjected to hydroprocessing as described in the section above entitled "*Hydroprocessing reactions*" and product(s) obtained from those reactions then subjected to catalytic cracking reactions to produce one or more desired hydrocarbon products.

In certain embodiments of the invention, hydroprocessing reactions may be performed on an oil of the invention (e.g. bio-oil, coal-oil or blended oil) to produce naphtha. The naphtha may then be subjected to steam cracking reactions to produce one or more desired hydrocarbon products.

Steam cracking reactions

In accordance with the methods of the present invention, feedstocks comprising hydrocarbons may be utilized in steam cracking reactions to produce target hydrocarbon product(s).

In preferred embodiments of the invention, naphtha produced by hydroprocessing an oil of the invention (e.g. bio-oil, coal-oil or blended oil) in accordance with the methods described in the section above entitled "*Hydroprocessing reactions*" may be used as a feedstock for steam cracking reactions to produce lower olefin hydrocarbon products.

Figure 5 shows a steam cracker configuration used to produce lower olefins from the naphtha produced from the bio-oil and/or coal oil containing feedstock in accordance with an exemplary embodiment of the invention. A naphtha steam cracker may be adapted to heat the naphtha with steam at high temperatures, (e.g. 850°C-1200°C) to crack the naphtha into smaller hydrocarbon compounds. The fresh feed 700 comprising at least in part naphtha produced from bio-oil and/or coal oil as described above may be fed with water into a pyrolysis heater 701. The water may be converted into steam and the naphtha is cracked into smaller hydrocarbon compounds. The different hydrocarbon compounds such as fuel oil, gasoline, methane, ethane, ethylene, LPG, propylene and C_4

products such as butylenes, can be separated in a series separation steps, for example, using a series of fractionators 702.

It will be understood that other known steam cracker configurations may be used to produce lower olefins from naphtha in accordance with the methods described herein.

Catalytic cracking reactions

In accordance with the methods of the present invention, feedstocks comprising hydrocarbons may be utilized in catalytic cracking reactions to produce target hydrocarbon product(s).

In other embodiments, an oil of the invention (e.g. bio-oil, coal-oil or blended oil) may be subjected to hydroprocessing as described in the section above entitled "*Hydroprocessing reactions*" and product(s) obtained from those reactions then subjected to catalytic cracking reactions to produce one or more desired hydrocarbon products.

For example, catalytic cracking reactions may be used to convert heavy hydrocarbon mixtures into gasoline and lower olefin products. The process may involve cracking the larger hydrocarbon compounds in the hydrocarbon-containing feedstock (i.e. "catalytic cracker feedstock") into the smaller valuable gasoline and/or lower olefin products in the presence of a hot fluid catalyst.

Catalytic cracking reactions may be performed in a catalytic cracker. Suitable configurations for a catalytic cracker that may be used include stacked type and side-by-side type catalytic crackers. The stacked type catalytic cracker may have a single container in which the reactor and catalytic regenerator are located. The reactor may be located above the catalytic regenerator. The side-by-side type catalytic cracker may be arranged such that the reactor and catalytic regenerator are located in separate containers. In accordance with the methods of the present invention, catalytic cracker feedstock is formed at least in part from bio-oil and/or coal oil. The bio-oil and/or coal oil may be used directly as at least part of the catalytic cracker feedstock or optionally be processed in a hydroprocessing reactor to remove oxygen, nitrogen and/or sulphur as (see section above entitled "*Hydroprocessing reactions*") prior to being used in the catalytic cracker feedstock.

Figure 6 shows an exemplary side-by-side type catalytic cracker configuration used to produce gasoline and /or lower olefins from a catalytic cracker feedstock. The catalytic cracker feedstock may be preheated to a temperature of between about 315 °C to about 430 °C and mixed with any recycled slurry oil from the bottom of the distillation column, used to separate the cracked hydrocarbon products following the catalytic cracking reactions, to form the total feed. The total feed may be injected into the catalyst riser 7 for vaporization and cracking into smaller hydrocarbon vapours. In the catalyst riser 7 the total feed is mixed with a very hot powdered catalyst from the regenerator. All of the cracking reactions can occur within the catalyst riser 7. The hydrocarbon vapors "fluidize" the powdered catalyst and the mixture of hydrocarbon vapors and catalyst may flow upward to enter the reactor at a temperature of about 535 °C and a pressure of about 1.72 barg or 1720 KPa.

In the reactor the cracked hydrocarbon product vapors and the spent catalyst may be separated. The separation may occur by passing the mixture of hydrocarbon vapors and catalyst through a set of two-stage cyclones 5 within the reactor. The spent catalyst can be returned to the catalyst regenerator via a steam stripping section to remove any hydrocarbon vapors.

The catalyst may be regenerated by burning off any deposited coke with air blown into the regenerator. The regenerator can operate at a temperature of about 715 °C and a pressure of about 2.41 barg or 2410 kPa. The combustion of the coke may be exothermic and it produces a large amount of heat that is partially absorbed by the regenerated catalyst and provides the heat required for the vaporization of the feedstock and the endothermic cracking reactions that take place in the catalyst riser.

The hot catalyst (at about 715°C) leaving the regenerator may flow into a catalyst withdrawal well 6 where any entrained combustion flue gases can be allowed to escape and flow back into the upper part to the regenerator. The flow of regenerated catalyst to the feedstock injection point below the catalyst riser can be regulated by a slide valve in the regenerated catalyst line. The hot flue gas exits the regenerator after passing through multiple sets of two-stage cyclones 5 that remove entrained catalyst from the flue gas.

The cracked hydrocarbon product vapors can be fed to a distillation column to separate the cracked hydrocarbon products. The different hydrocarbon fractions can then be collected such as fuel oil and gasoline. Some fractions may be further processed to produce various hydrocarbon products (e.g. lower olefins such as propylene and butylene).

In certain embodiments, an oil of the invention (e.g. bio-oil, coal-oil or blended oil) may be subjected to catalytic cracking reactions to produce one or more desired hydrocarbon products without a performing a preceding hydroprocessing step. Accordingly, catalytic cracking reactions may be performed directly on an oil of the invention (e.g. bio-oil, coal-oil or blended oil) to produce target hydrocarbon product(s) (e.g. gasoline and/or lower olefins).

It will be understood that any known catalytic cracker configuration may be used to produce hydrocarbon products such as gasoline and lower olefins from catalytic cracker feedstock derived from oils of the invention (e.g. bio-oil, coal-oil or blended oil).

Exemplary processes

A description of methods according to various embodiments of the invention is provided below. It will be understood that the invention is not limited to the specific embodiments described.

Figure 7a shows a method for producing lower olefins from biomass according to an embodiment of the invention. Biomass 50 may be processed into bio-oil 60, for example, by a fast pyrolysis reaction or a thermochemical reaction as described above in the section entitled "*Oil production*". The bio-oil 60 may then be processed in a hydroprocessing reaction (see section above entitled "*Hydroprocessing reactions*") to produce naphtha 70. The naphtha 70 may then be used as a substrate for steam cracking reactions (see section above entitled "*Cracking reactions*") to produce lower olefins 80. The lower olefins 80 can be processed into plastics and/or other chemicals.

Figure 7b shows a method of producing lower olefins from coal according to another embodiment of the invention. Coal 100 may be processed into coal-oil 110, for example, by a fast pyrolysis reaction or a thermochemical reaction as described above in the section entitled "*Oil production*". The coal-oil 110 may then be processed in a hydroprocessing reaction (see section above entitled "*Hydroprocessing reactions*") to produce naphtha 70. The naphtha 70 may then be used as a substrate for steam cracking reactions to produce lower olefins 80 (see section above entitled "*Cracking reactions*"). The lower olefins 80 can then be processed into plastics and/or other chemicals 100.

In a further embodiment of the invention, naphtha is produced from a blended oil of the invention (for example, a bio-oil combined with a coal oil, or, a bio-oil and/or coal oil combined with crude oil). The blended oil may optionally be mixed with a gas condensate (see section above entitled "*Hydroprocessing reactions*"). The oil may be processed in a hydroprocessing reaction (see section above entitled "*Hydroprocessing reactions*") to produce naphtha 70. The naphtha 70 may then be used as a substrate for steam cracking reactions to produce lower olefins 80 (see section above entitled "*Cracking reactions*"). The lower olefins 80 can then be processed into plastics and/or other chemicals 100.

Accordingly, certain embodiments of the invention enable biomass and/or coal, including brown coal, to be processed to produce a naphtha intermediate which can then be used as a feedstock to produce hydrocarbon products such as lower olefins.

The lower olefin hydrocarbon products such as ethylene, propylene and butylene may then be used to produce a wide variety of products such as plastics, polyethylene, polypropylene, synthetic rubber and adhesives by catalytic polymerization. Lower olefins such as ethylene and propylene may also be processed to produce organic chemicals such as ethylene oxide and acrolein which form the basis for many chemical products. Ethylene oxide and acrolein can be produced by oxidation of ethylene and propylene, respectively. Ethylene oxide can be used as an ingredient in many surfactant and detergent compositions to produce ethylene glycol and other glycol esters. Acrolein can be used in the preparation of polyester resin, polyurethane, propylene glycol, acrylic acid, acrylonitrile, and glycerol.

Figure 8a shows a method of producing gasoline and optionally lower olefins from biomass according to an additional embodiment of the invention. Biomass 50 may be processed into bio-oil 60, for example, by a fast pyrolysis reaction or a thermochemical reaction as described above in the section entitled "*Oil production*". The bio-oil 60 may then be used (without hydroprocessing) in a catalytic cracker feedstock 40. The catalytic cracker feedstock 40 may be used as a substrate in catalytic cracker reactions (see section above entitled "*Cracking reactions*") to produce gasoline 70 and/or lower olefins 80. The lower olefins 80 may be processed into plastics and/or other organic chemicals 100. Optionally, the bio-oil 60 may be pre-processed in a hydroprocessing reaction (see section above entitled "*Hydroprocessing reactions*") to form a higher quality catalytic cracker feedstock 40 prior to use as a substrate for the catalytic cracking reactions. The hydroprocessing reactions may produce some gasoline 70 and/or lower olefin products 80 directly from the oil. The heavy products produced from the hydroprocessing reaction can be used as the catalytic cracker feedstock 40 for catalytic cracker reactions to produce gasoline 70 and/or lower olefins 80.

Figure 8b shows a method of producing gasoline and optionally lower olefins from coal according to an additional embodiment of the invention. Coal 100 may be processed into coal-oil 110, for example, by a fast pyrolysis reaction or a thermochemical reaction as described above in the section entitled "*Oil production*". The coal oil 110 may be used (without hydroprocessing) in a catalytic cracker feedstock 40. The catalytic cracker feedstock 40 may be used as a substrate in catalytic cracker reactions (see section above entitled "*Cracking reactions*") to produce gasoline 70 and/or lower olefins 80. The lower olefins 80 may be processed into plastics and/or other chemicals 90. Optionally, the coal-oil 110 may be pre-processed in a hydroprocessing reaction (see section above entitled "*Hydroprocessing reactions*") to form a higher quality catalytic cracker feedstock 40 prior to use as a substrate for the catalytic cracking reactions. The hydroprocessing reactions may produce some gasoline 70 and/or lower olefin products 80 directly from the oil. The heavy products produced from the hydroprocessing reaction can be used as the catalytic cracker feedstock 40 for catalytic cracker reactions to produce gasoline 70 and/or lower olefins 80.

In a further embodiment of the invention, the cracker feedstock 40 used as a substrate in the catalytic cracking reactions may be produced from or comprise a blended oil of the invention (for example, a bio-oil combined with a coal oil, or, a bio-oil and/or coal oil combined with crude oil). The blended oil may optionally be mixed with a gas condensate (see section above entitled "*Hydroprocessing reactions*"). Optionally, the oil may be pre-processed in a hydroprocessing reaction (see section above entitled "*Hydroprocessing reactions*") to form a higher quality catalytic cracker feedstock 40 prior to use as a substrate for the catalytic cracking reactions. The hydroprocessing reactions may produce some gasoline 70 and/or lower olefin products 80 directly from the oil. The heavy products produced from the hydroprocessing reaction can be used as catalytic cracker feedstock 40 for catalytic cracker reactions to produce gasoline 70 and/or lower olefins 80.

Accordingly, certain embodiments of the invention enable biomass and/or coal, including brown coal, to be processed to produce hydrocarbon products such as gasoline and/or lower olefins by using bio-oil and/or coal-oil produced from biomass and/or coal in catalytic cracking reactions, hydroprocessing reactions, or both.

The lower olefin hydrocarbon products such as, for example, ethylene, propylene, butylenes, butadiene and isoprene and other similar olefins may provide the building blocks from which a wide variety of polymeric products can be manufactured by catalytic polymerization (e.g. polyethylene, polypropylene, synthetic rubber and adhesives). Lower olefins such as ethylene and propylene may also be processed to produce organic chemicals such as ethylene oxide and acrolein which form the basis for many chemical products. Ethylene is one of the more commonly produced organic compounds in the world and forms the basis of a vast range of compositions and materials. Ethylene oxide and acrolein can be produced by oxidation of ethylene and propylene, respectively. Ethylene oxide can be used as an ingredient in many surfactant and detergent compositions to produce ethylene glycol and other glycol esters. Acrolein can be used in the preparation of polyester resin, polyurethane, propylene glycol, acrylic acid, acrylonitrile, and glycerol.

Gasoline hydrocarbon products (e.g. C_3-C_{12}, more preferably C_4 to about C_{10}) may be collected and used directly as fuel and/or be further processed, for example, to produce upgraded fuels (e.g. jet fuel).

Renewable hydrocarbon products

The present invention provides methods for producing renewable hydrocarbon products (e.g. gasoline and lower olefins). The production of renewable hydrocarbon products may reduce the adverse environment effects and/or economic costs in comparison to existing technologies which rely on the extraction and use of crude oil. For example, when bio-oil is used as feedstock or a portion of feedstock for hydroprocessing reactions and/or cracking reactions in accordance with the methods of the invention, the hydrocarbon products that are produced from a feedstock comprising x% bio-oil feedstock are considered to be x% renewable products.

one embodiment, the feedstock is comprised of at least 50% of the bio-oil and the hydrocarbon product is at least a 50% renewable product.

In another embodiment, the feedstock is comprised of at least 75% of the bio-oil and the hydrocarbon product is at least a 75% renewable product.

In one embodiment, the feedstock is comprised of at least 90% of the bio-oil and the hydrocarbon product is at least a 90% renewable product.

In one embodiment, the feedstock is comprised of at least 95% of the bio-oil and the hydrocarbon product is at least a 95% renewable product.

In one embodiment, the feedstock is comprised of at least 98% of the bio-oil and the hydrocarbon product is at least a 98% renewable product.

In one embodiment, the feedstock is 100% bio-oil and the hydrocarbon product is a 100% renewable product.

In certain embodiments, the invention enables biomass and/or coal (e.g. lignite) to be processed to produce gasoline and/or lower olefins. Thus, the present methods enable fuel, high volume polymers and/or chemical products to be manufactured from non-crude oil sources that are either renewable when sourced from biomass or available in large qualities globally when sourced from coal.

In other embodiments of the invention, feedstock for use in hydroprocessing reactions and/or cracking reactions in accordance with the methods of the invention may comprise a mixture of bio-oil with fossil oil (e.g. crude oil and/or coal-oil) and/or gas condensate. For example, the bio-oil may be mixed in with 0% to 99% by weight of fossil oil, and/or coal oil, and/or gas condensate. If x% of bio-oil is utilized in a feedstock for hydroprocessing reactions and/or cracking reactions then the hydrocarbon products, (e.g. naphtha, gasoline, lower olefins) are considered to be x% renewable hydrocarbon products. Coal oil may also be mixed with crude oil and/or gas condensate to form a mixed catalytic cracker feedstock.

It will be appreciated by persons skilled in the art that numerous variations and/or modifications may be made to the invention as shown in the specific embodiments without departing from the spirit or scope of the invention as broadly described. The present embodiments are, therefore, to be considered in all respects as illustrative and not restrictive.

EXAMPLES

The invention will now be described with reference to specific examples, which should not be construed as in any way limiting.

Example 1: Catalytic cracking of lignite and bio-oil syncrudes

Figure 9 shows a schematic of a Micro Activity Test (MAT) unit comprising a fixed bed of catalyst contained in a Pyrex glass reactor supported in a temperature controlled furnace. The lignite and bio-oil syncrudes were used as feeds to the MAT unit as follows:

Condensate (lignite oil)	Syncrude (Bio-oil)
100	0
90	10
70	30

The MAT unit that was operated at the conditions shown below:

Contact Time (TOS): 30 seconds
Catalyst to Oil Ratio (CTO): 2-6 (WHSV = 20-60h^{-1})
Temperature = 500°C
Catalytic Cracking Equilibrium Catalyst:
surface area 290 m^2/g; ~30% zeolite Y with a unit cell dimension (UCS) of 24.28 Å

The catalyst was charged to the reactor and preheated under nitrogen flow. The catalyst was an equilibrium sample with the properties given above.

The syncrude feeds were injected at a controlled rate using a syringe pump. Following the feed injection cycle, remaining hydrocarbons are stripped from the catalyst bed and reactor by continuing nitrogen purge. Liquid syncrude products were collected in a cold receiver, and total gas volume was determined by water displacement. Gas and syncrude products i.e. gasoline and light cycle oil (LCO) were analyzed by gas chromatography, and the spent catalyst was analyzed to determine coke deposition.

The results were material balanced to generate a full slate of yields, with liquid product boiling range determined from the GC simulated distillation.

(i) Syncrude Feed Analyses

Carbon, Hydrogen, Nitrogen, Sulfur and Oxygen content (%w) and dry calorific values (MJ/kg) of lignite syncrude and bio-oil syncrude are shown in **Table 1** below.

Table 1

Sample	**C**	**H**	**N**	**S**	**O**	**Dry Calorific Value (MJ/kg)**
Lignite syncrude	80.9	8.7	0.18	0.17	10.05	36.5
Bio-oil syncrude	80.8	7.5	0.01	0.06	11.63	34.2

Note:

(i) oxygen content calculated by difference

(ii) Lignite and Bio-oil syncrudes were produced according to the process described in the following patent applications: PCT/AU2008/000429; PCT/AU2009/001260 and PCT/AU2009/001312 (the contents of each of these 3 patent applications are incorporated herein by cross-reference in their entirety)

(iii) The lignite syncrude was produced using a sample of lignite from the Yaloorn deposit in Victoria, Australia

(iv) The bio-oil syncrude was produced using a sample of pinus radiata biomass from NSW, Australia

(ii) H^1 NMR spectrum of lignite syncrude

The H^1 NMR spectrums of lignite and bio-oil syncrudes are shown in **Figures 10 and 11** respectively. The spectrums demonstrate that the chemical compositions are primarily composed of single ring aromatic and alkane chain structures with negligible polyaromatic compounds. Based on this analysis it may be predicted that the syncrude oils with this composition can be readily processed in either a catalytic cracker (preferably with a pre-hydrotreating step) or a hydroprocessing plant to transportation fuels. The laboratory testing data below show that the lignite and bio-oil syncrudes can indeed be readily processed in a catalytic cracker to produce gasoline.

(iii) Catalytic cracking conversion of lignite and bio-oil syncrude mixtures in the MAT unit

Figure 12 shows conversion (wt%) of lignite and bio-oil syncrude mixtures to all products which include gasoline, LCO, gas and coke.

(iv) Catalytic cracking product yields of lignite and bio-oil syncrude mixtures in the MAT unit

Figure 13 shows product yields (wt%) of gasoline, light cycle oil (LCO), gases and coke from lignite and bio-oil syncrude mixtures.

(v) Catalytic cracking gas yields of lignite and bio-oil syncrude mixtures in the MAT unit

Figure 14 shows gas yields (wt%) of propylene/TC3, butene/TC4, C1 and C2 carbons, and isobutene/isobutane from lignite and bio-oil syncrude mixtures.

Although these results demonstrate that lignite and bio-oil syncrudes can be directly catalytically cracked to, for example, gasoline and LCO, processing may include a pre-hydrotreatment of the syncrudes to reduce the heteroatoms such as S, N and O which may significantly improve the quality of the gasoline and LCO produced.

CLAIMS:

1. A method for producing a hydrocarbon product from coal comprising the following steps:

converting the coal to a coal-oil by thermal or hydrothermal conversion;

processing the coal-oil in a hydroprocessing reaction to remove one or more of oxygen, nitrogen or sulfur from hydrocarbon compounds in the coal-oil; and

using at least a portion of the coal-oil as a feedstock in a cracking reaction to convert hydrocarbon compounds in the feedstock into a mixture of smaller hydrocarbon compounds comprising the hydrocarbon product.

2. A method for producing a hydrocarbon product from biomass comprising the following steps:

converting the biomass to bio-oil by thermal or hydrothermal conversion;

processing the bio-oil in a hydroprocessing reaction to remove one or more of oxygen, nitrogen or sulfur from hydrocarbon compounds in the bio-oil; and

using at least a portion of the bio-oil as a feedstock in a cracking reaction to convert hydrocarbon compounds in the feedstock into a mixture of smaller hydrocarbon compounds comprising the hydrocarbon product.

3. The method of claim 2, wherein the feedstock is comprised of at least 50% of said bio-oil and said hydrocarbon product is at least a 50% renewable product.

4. The method of claim 2 or claim 3, wherein the feedstock is comprised of at least 75% of said bio-oil and said hydrocarbon product is at least a 75% renewable product.

5. The method of claim 2 or claim 3, wherein the feedstock is comprised of at least 90% of said bio-oil and said hydrocarbon product is at least a 90% renewable product.

6. The method of any one of claims 1 to 5, wherein said converting is by fast pyrolysis reaction.

7. The method of any one of claims 1 to 6, wherein the cracking reaction is a catalytic cracking reaction utilizing a powdered catalyst at a reaction temperature of

between about 500°C and 600°C, and a reaction pressure of between about 1400 KPa and 2000 KPa.

8. The method of any one of claims 1 to 7, wherein the cracking reaction is a catalytic cracking reaction utilized to convert hydrocarbons of C_{12} or above into a hydrocarbon product selected from any one or more of gasoline and fuel oil.

9. The method of any one of claims 1 to 7, wherein said hydroprocessing reaction additionally produces a hydrocarbon product selected from any one or more of a gasoline, lower olefins, and naphtha.

10. The method of any one of claims 1 to 9, wherein said hydroprocessing reaction produces a naphtha intermediate.

11. The method of claim 10, wherein the cracking reaction is a steam cracking reaction utilizing steam at a reaction temperature of between about 850°C and about 1200°C to convert the naphtha into a hydrocarbon product selected from any one or more of fuel oil, gasoline, methane, ethane, LPG, and lower olefins.

12. The method of claim 11, wherein the lower olefins are selected from any one or more of ethylene, propylene, butylenes and combinations thereof.

13. The method of any one of claims 1 to 12, comprising the additional step of catalytically polymerizing the lower olefins, wherein said polymerizing produces a product selected from any one or more of plastic, polyethylene, polypropylene, synthetic rubber and adhesives.

14. The method of any one of claims 1 to 12, comprising the additional step of oxidizing the lower olefins, wherein said oxidising produces an organic chemical product selected from any one or more of ethylene oxide and acrolein.

15. The method of any one of claims 1 to 14, wherein the hydroprocessing reaction is a catalytic hydroprocessing reaction utilising a catalyst comprising an active metal or a combination of active metals.

16. The method of claim 15, wherein the catalyst comprises at least one group VIB metal, at least one metal group VIII metal, or a combination thereof.

17. The method of claim 15 or claim 16, wherein the catalyst is at least one of a cobalt-molybdenum (CoMo), nickel-molybdenum (NiMo) or nickel-tungsten (NiW) type catalyst.

18. The method according to any one of claims 1 to 17, wherein the hydroprocessing reaction is performed in a hydroprocessing plant and produces C_1 - C_4 hydrocarbons, and wherein said C_1 - C_4 hydrocarbons are used as a fuel source for burners in said hydroprocessing plant.

19. The method of any one of claims 1 to 18, wherein the hydroprocessing reaction is performed in a single stage hydroprocessing plant or two-stage hydroprocessing plant.

20. The method of any one of claims 1 to 18, wherein the hydroprocessing reaction is performed in a multi-bed hydroprocessing plant or a series flow hydroprocessing plant.

21. The method of any one of claims 18 to 20, wherein the hydroprocessing plant is integrated with a methanol plant, hydrogen produced from methanol plant is fed to the hydroprocessing plant for use in the catalytic hydroprocessing reaction, and C_1 to C_4 hydrocarbons produced from the hydroprocessing reaction are used as a feedstock for the methanol plant.

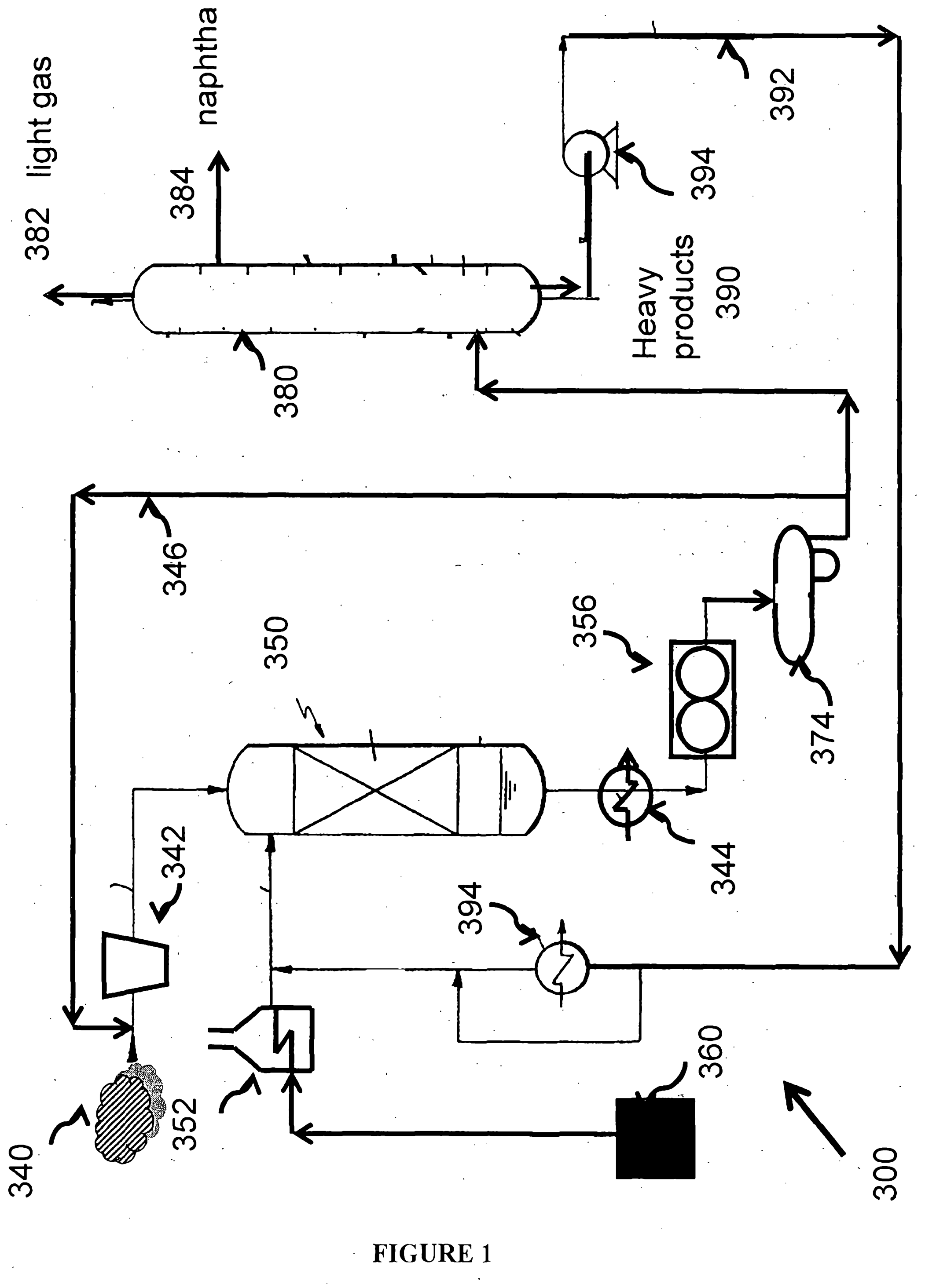
382 light gas
384 naphtha
380
Heavy products 390
394
392
346
350
356
374
342
344
394
340
352
360
300

FIGURE 1

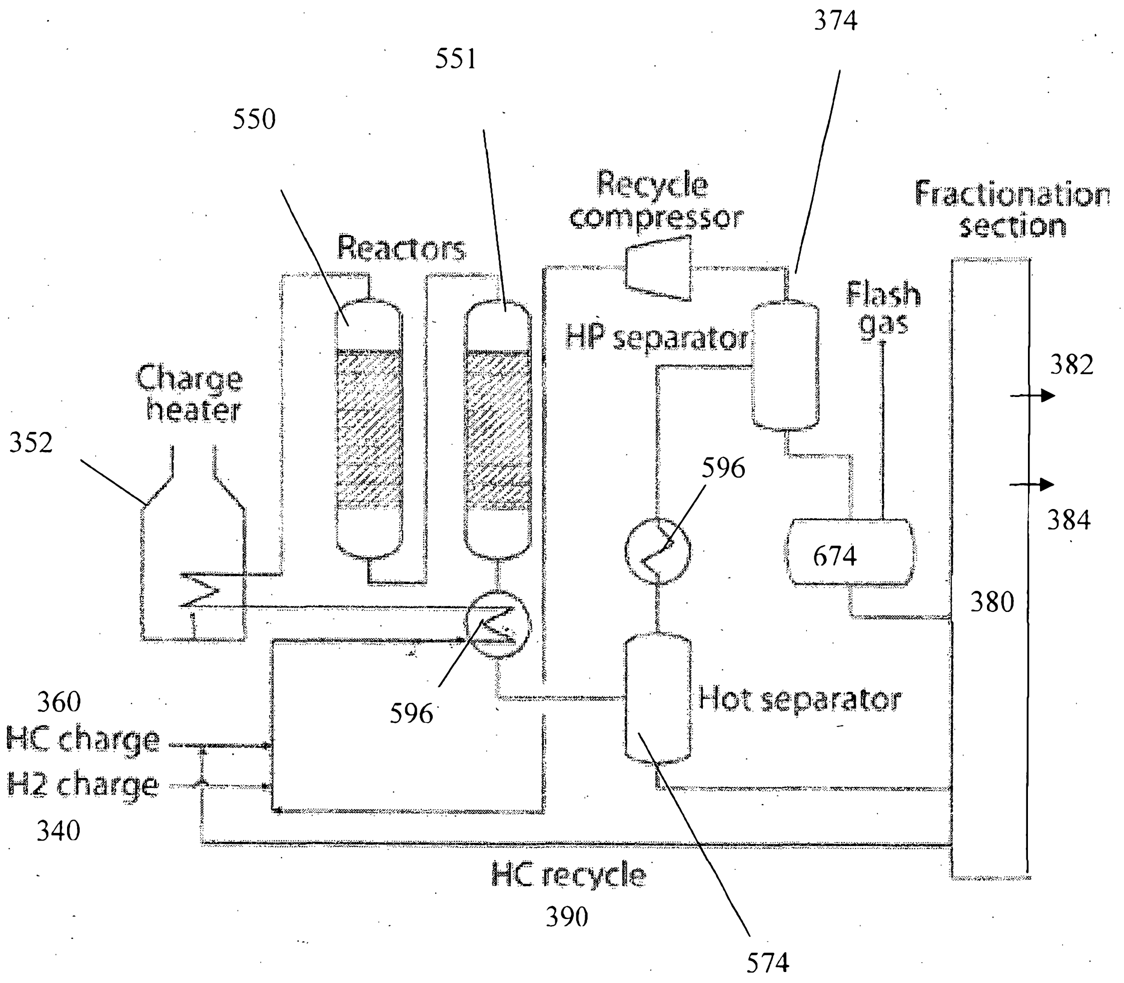
374
551
550
Recycle compressor
Fractionation section
Reactors
Flash gas
HP separator
Charge heater
382
352
596
384
674
380
Hot separator
360
HC charge
596
H2 charge
340
HC recycle
390
574

FIGURE 2

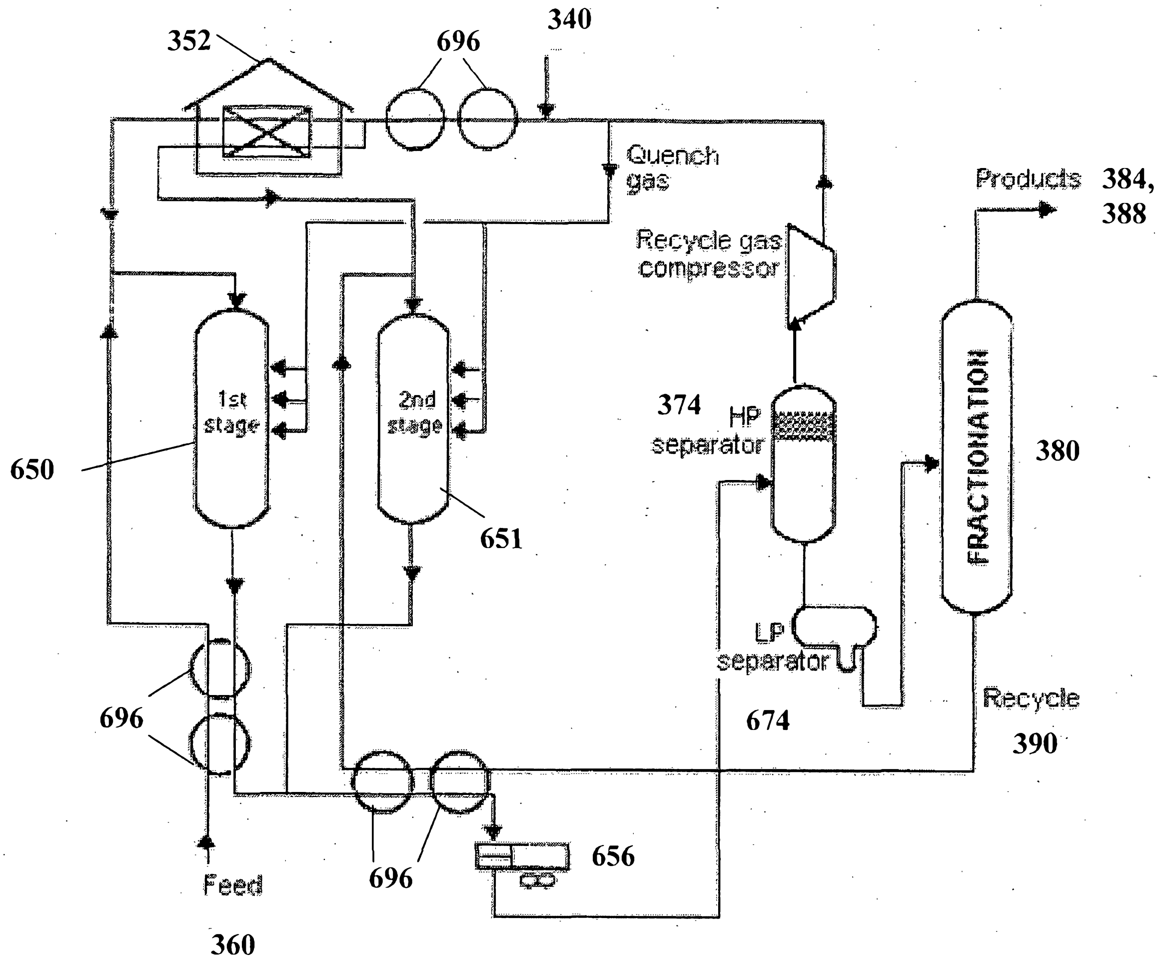
352
696
340
Quench gas
Products 384, 388
Recycle gas compressor
1st stage
2nd stage
374 HP separator
FRACTIONATION
380
650
651
LP separator
674
Recycle
390
696
696
656
Feed
360

FIGURE 3

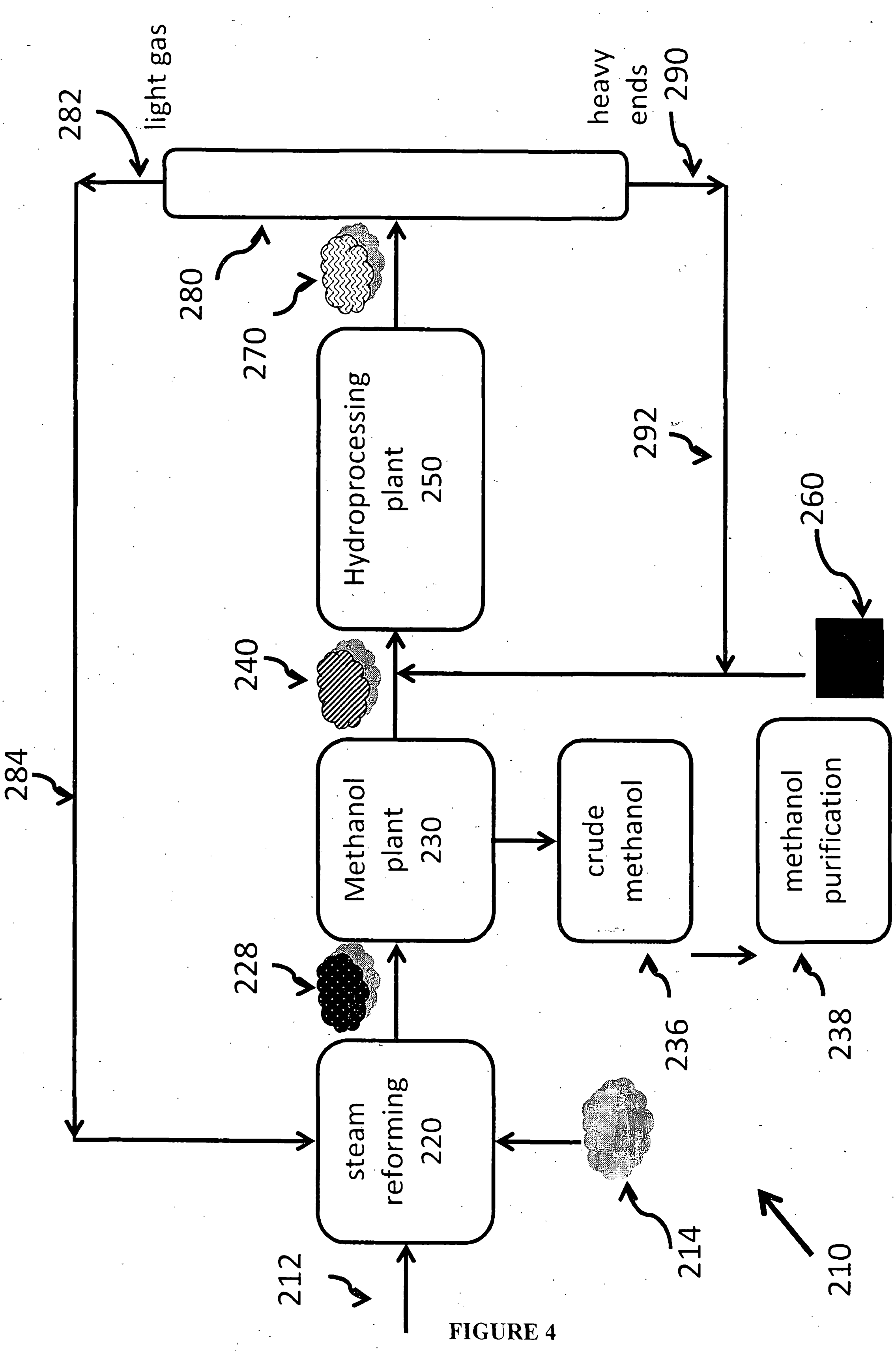
light gas
282
heavy ends
290
280
270
Hydroprocessing plant 250
292
260
240
284
Methanol plant 230
crude methanol
methanol purification
228
236
238
steam reforming 220
212
214
210

FIGURE 4

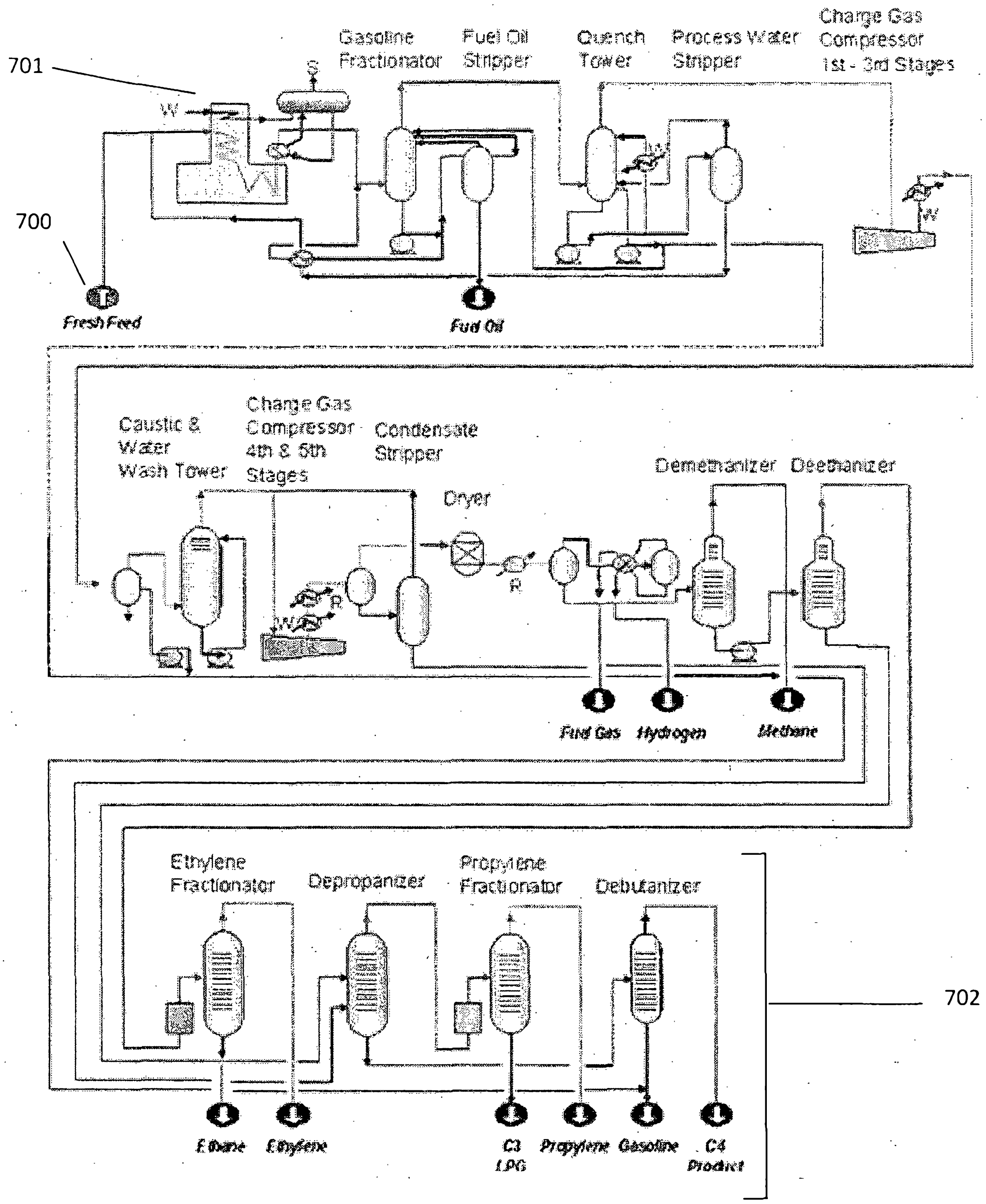
701
W
S
Gasoline Fractionator
Fuel Oil Stripper
Quench Tower
Process Water Stripper
Charge Gas Compressor 1st - 3rd Stages
W
W
700
Fresh Feed
Fuel Oil
Caustic & Water Wash Tower
Charge Gas Compressor 4th & 5th Stages
Condensate Stripper
Dryer
R
W
R
Demethanizer
Deethanizer
Fuel Gas
Hydrogen
Methane
Ethylene Fractionator
Depropanizer
Propylene Fractionator
Debutanizer
702
Ethane
Ethylene
C3 LPG
Propylene
Gasoline
C4 Product

FIGURE 5

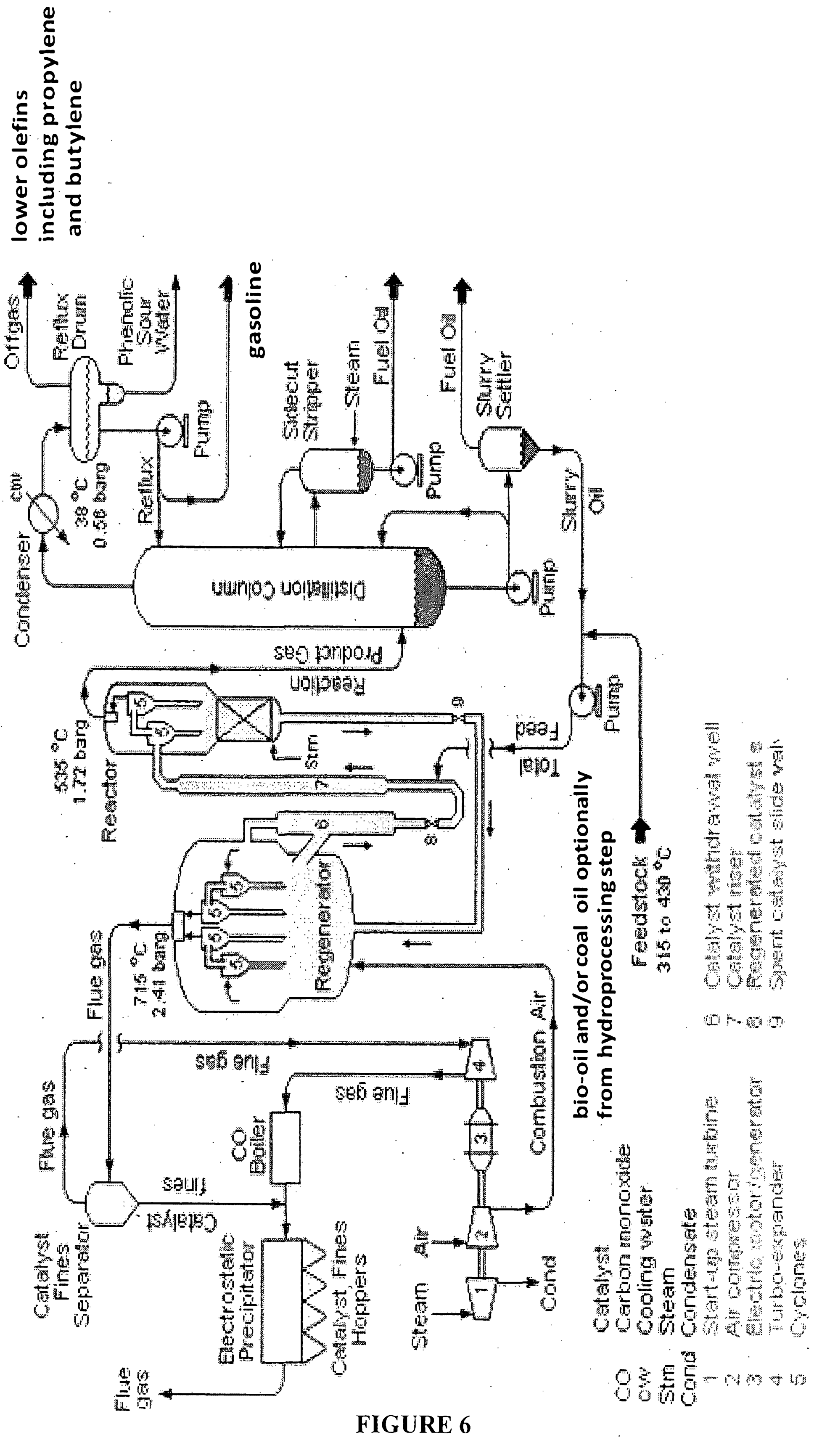
lower olefins including propylene and butylene
Offgas
Reflux Drum
Phenolic Sour Water
gasoline
Sidecut Stripper
Steam
Fuel Oil
Fuel Oil
Slurry Settler
Condenser
cw
38 °C
0.56 barg
Reflux
Pump
Pump
Distillation Column
Pump
Slurry Oil
Product Gas
Reaction
535 °C
1.72 barg
Reactor
Stm
Total Feed
Pump
Flue gas
715 °C
2.41 barg
Regenerator
bio-oil and/or coal oil optionally from hydroprocessing step
Feedstock 315 to 430 °C
Catalyst Fines Separator
Flue gas
Catalyst fines
Flue gas
Flue gas
CO Boiler
Combustion Air
Electrostatic Precipitator
Catalyst Fines Hoppers
Flue gas
Steam
Air
Cond
1
2
3
4
5
6
7
8
9
Catalyst
CO Carbon monoxide
cw Cooling water
Stm Steam
Cond Condensate
1 Start-up steam turbine
2 Air compressor
3 Electric motor/generator
4 Turbo-expander
5 Cyclones
6 Catalyst withdrawal well
7 Catalyst riser
8 Regenerated catalyst s
9 Spent catalyst slide valv

FIGURE 6

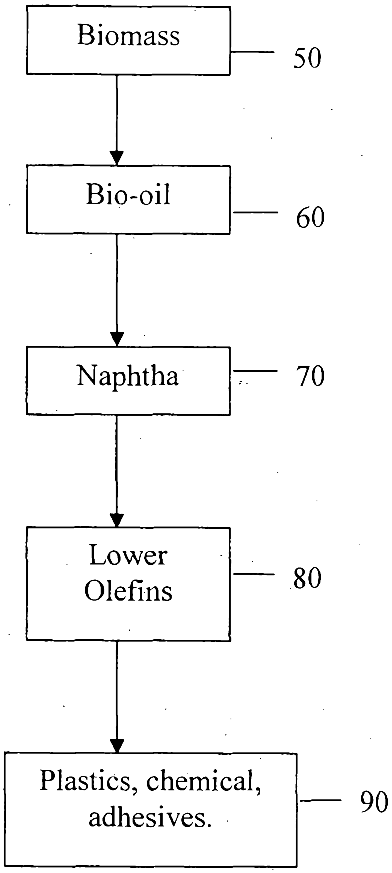

FIGURE 7A

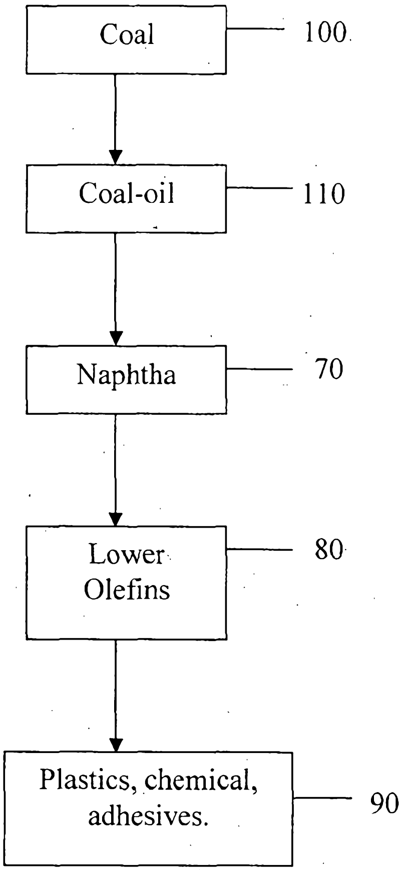

FIGURE 7B

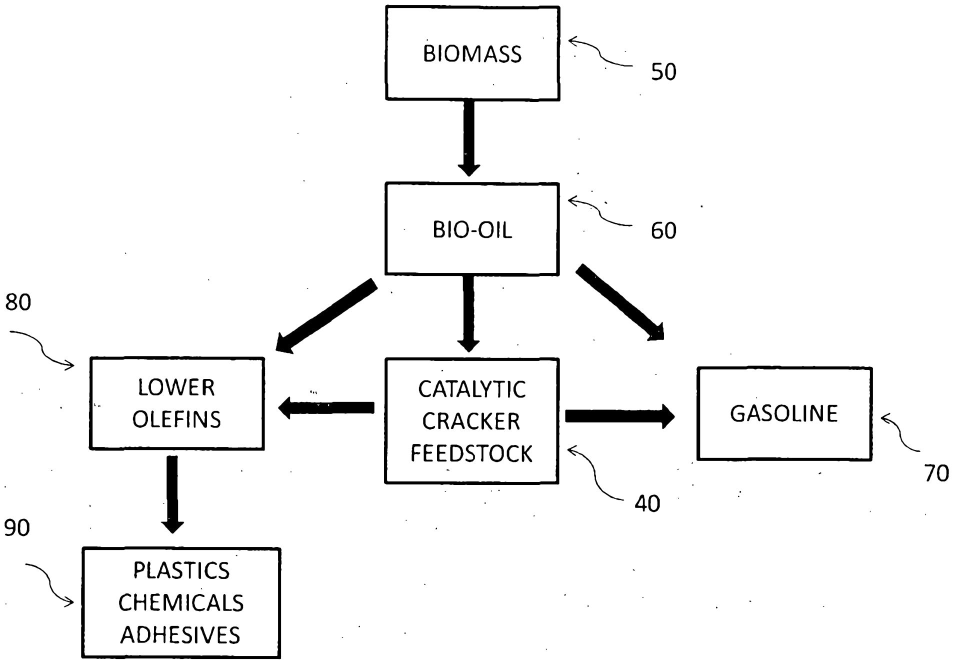

FIGURE 8A

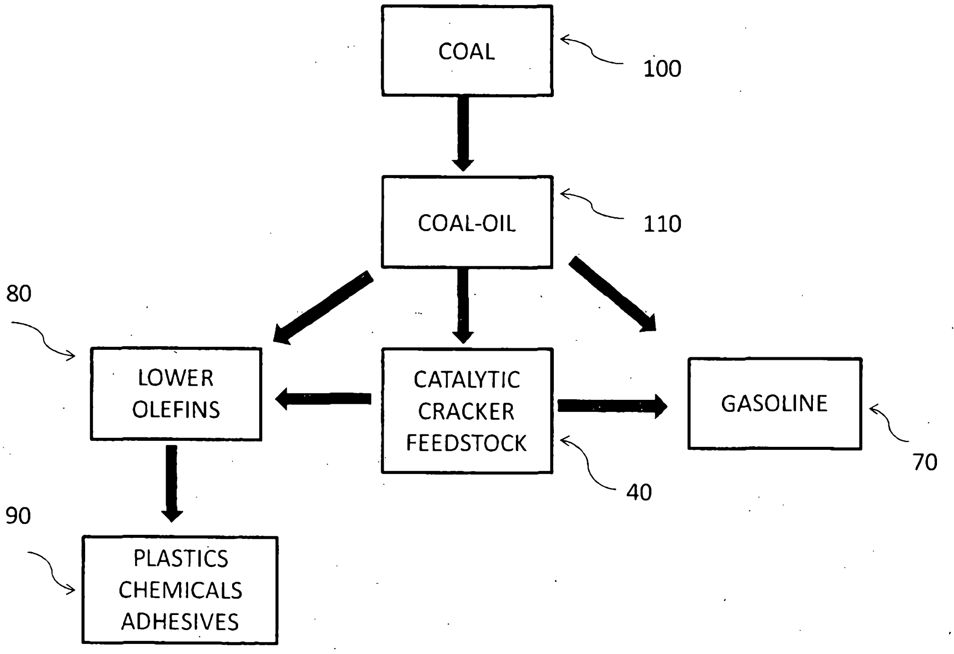

FIGURE 8B

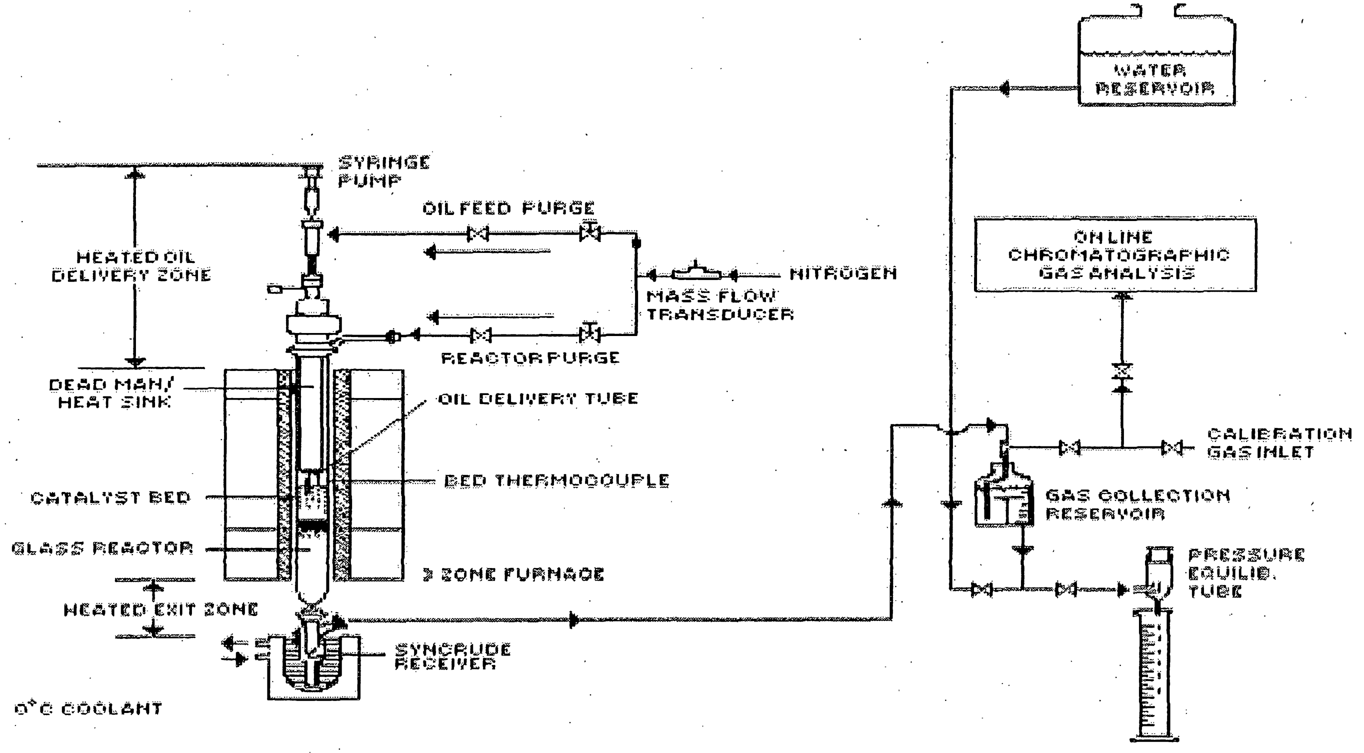
SYRINGE PUMP
HEATED OIL DELIVERY ZONE
OIL FEED PURGE
NITROGEN
MASS FLOW TRANSDUCER
REACTOR PURGE
DEAD MAN/ HEAT SINK
OIL DELIVERY TUBE
BED THERMOCOUPLE
CATALYST BED
GLASS REACTOR
3 ZONE FURNACE
HEATED EXIT ZONE
SYNCRUDE RECEIVER
0°C COOLANT
WATER RESERVOIR
ONLINE CHROMATOGRAPHIC GAS ANALYSIS
CALIBRATION GAS INLET
GAS COLLECTION RESERVOIR
PRESSURE EQUILIB. TUBE

FIGURE 9

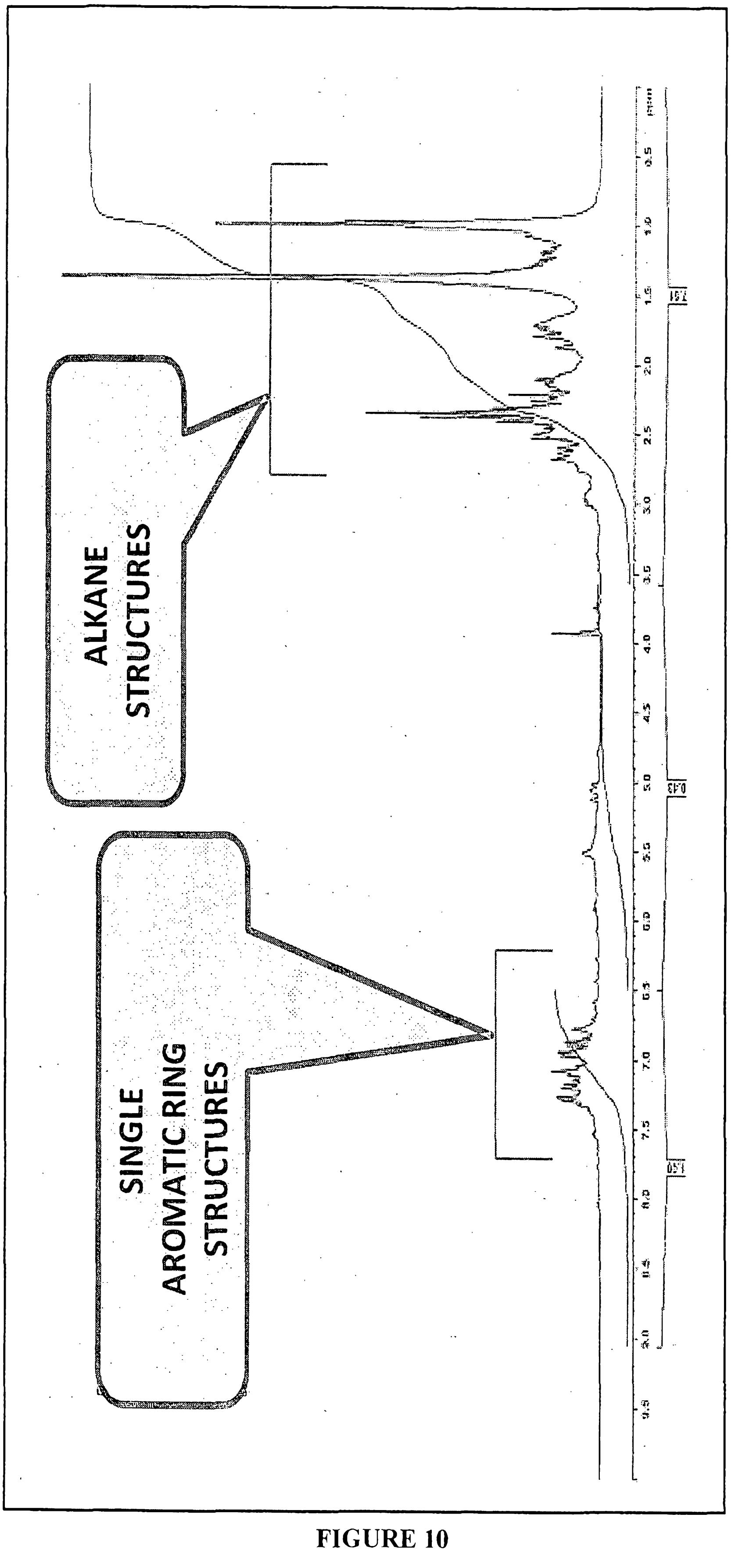
ALKANE STRUCTURES
SINGLE AROMATIC RING STRUCTURES
ppm
0.5
1.0
1.5
2.0
2.5
3.0
3.5
4.0
4.5
5.0
5.5
6.0
6.5
7.0
7.5
8.0
8.5
9.0
9.5
7.91
0.43
1.50

FIGURE 10

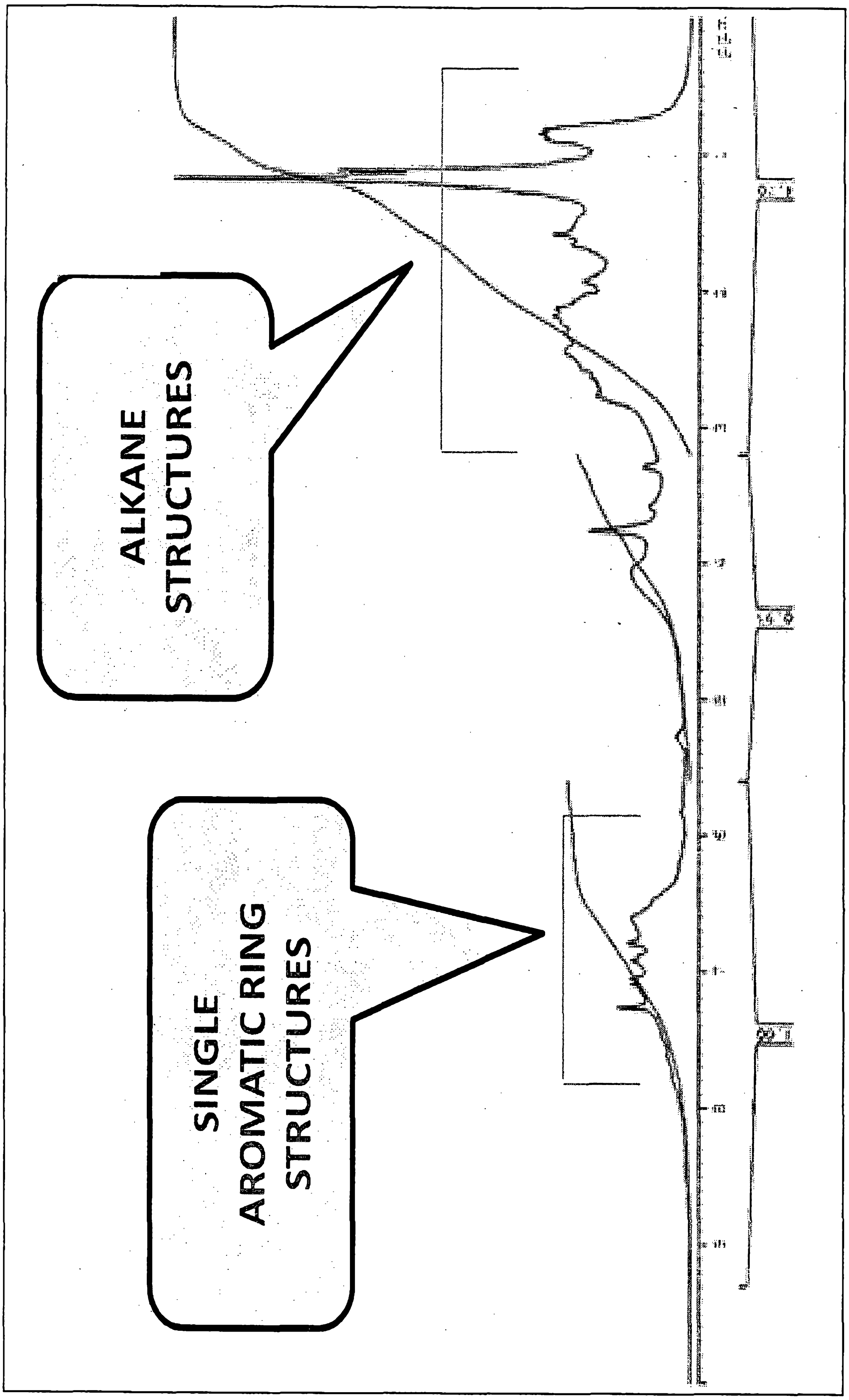

FIGURE 11

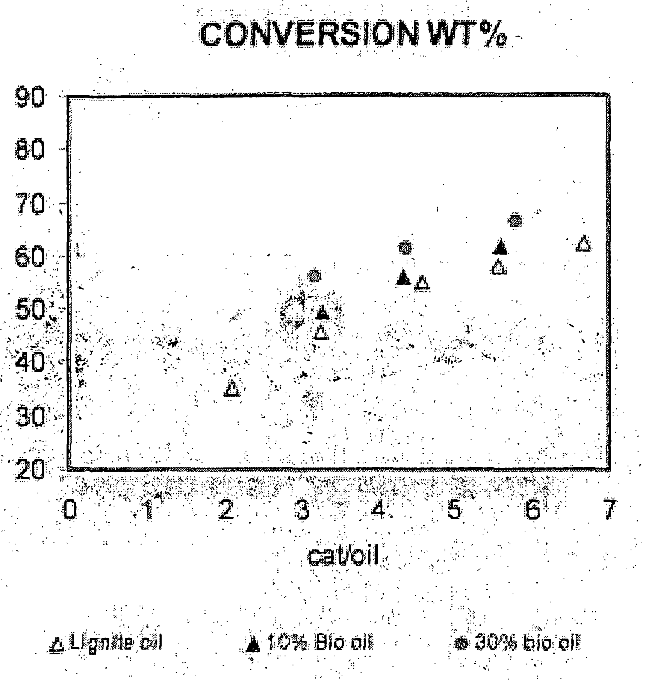
CONVERSION WT%
90
80
70
60
50
40
30
20
0
1
2
3
4
5
6
7
cat/oil
△ Lignite oil
▲ 10% Bio oil
● 30% bio oil

FIGURE 12

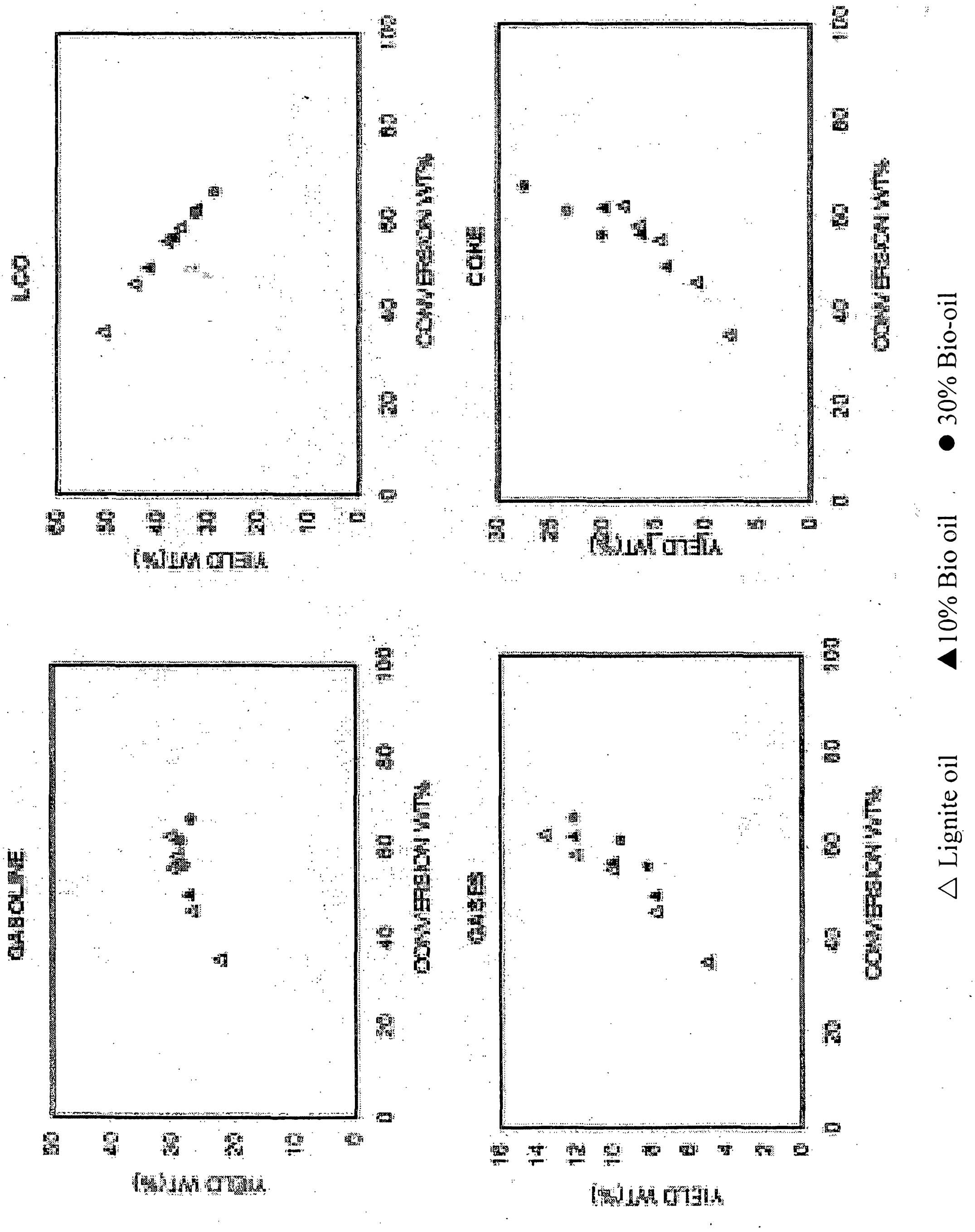
GASES
YIELD WT(%)
16
14
12
10
8
6
4
2
0
CONVERSION WT%
0
20
40
60
80
100
GASOLINE
YIELD WT(%)
50
40
30
20
10
0
CONVERSION WT%
0
20
40
60
80
100
COKE
YIELD WT(%)
30
25
20
15
10
5
0
CONVERSION WT%
0
20
40
60
80
100
LCO
YIELD WT(%)
60
50
40
30
20
10
0
CONVERSION WT%
0
20
40
60
80
100
△ Lignite oil
▲10% Bio oil
● 30% Bio-oil

FIGURE 13

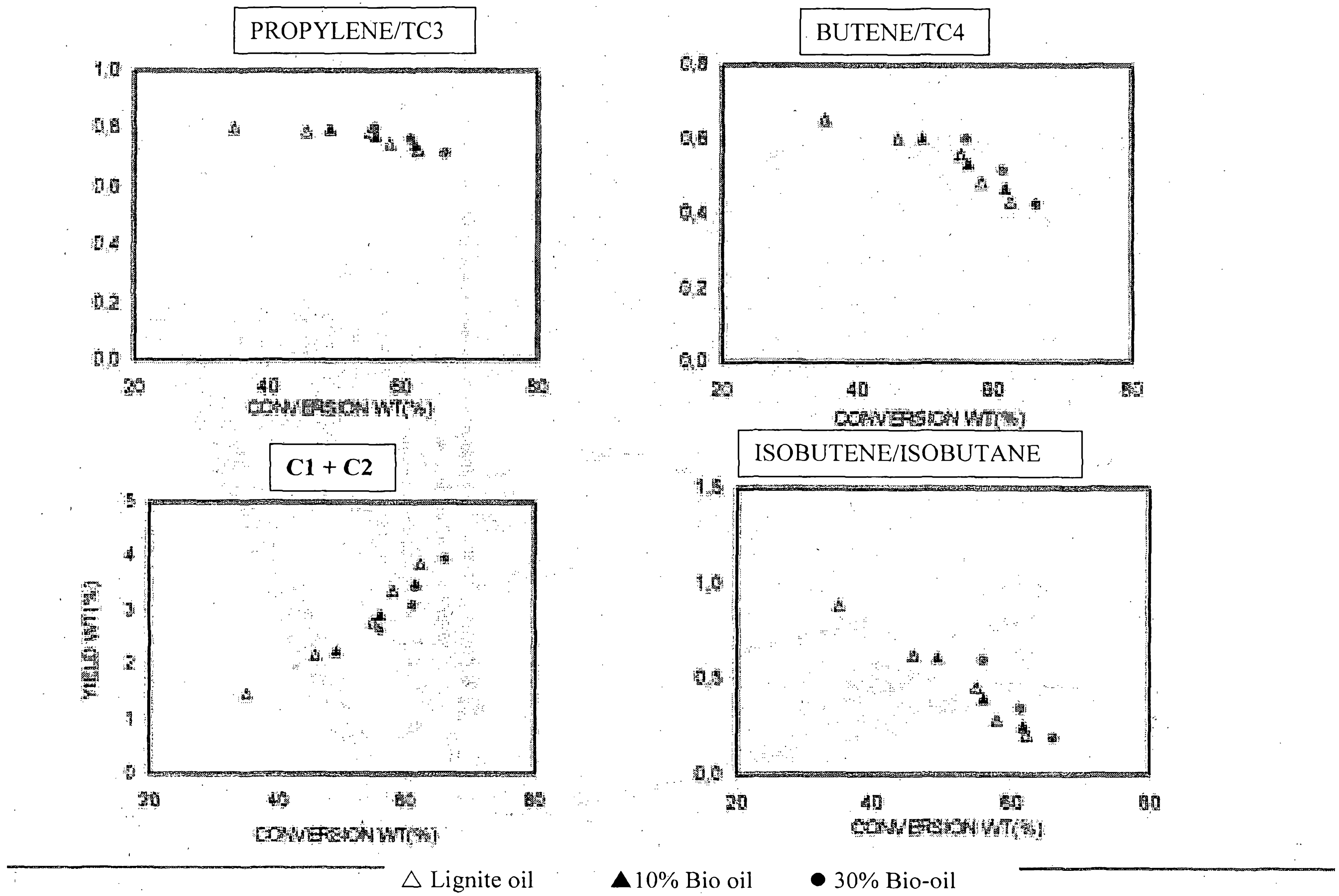
PROPYLENE/TC3
1.0
0.8
0.6
0.4
0.2
0.0
20
40
60
80
CONVERSION WT(%)
BUTENE/TC4
0.8
0.6
0.4
0.2
0.0
20
40
60
80
CONVERSION WT(%)
C1 + C2
5
4
3
2
1
0
YIELD WT(%)
20
40
60
80
CONVERSION WT(%)
ISOBUTENE/ISOBUTANE
1.5
1.0
0.5
0.0
20
40
60
80
CONVERSION WT(%)
△ Lignite oil
▲10% Bio oil
● 30% Bio-oil

FIGURE 14