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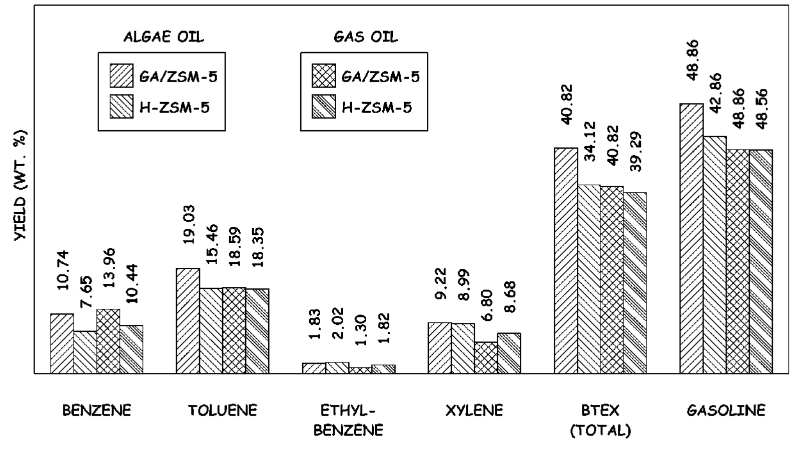

Fig. 10

(57) Abstract: Renewable oils are converted to aromatics, by contact with a catalytically-active form of gallium, for use in the petrochemical industry and/or for fuel blending components or additives. The renewable oil(s) feature high oxygen content, high H/C mole ratios, and high fatty acid or fatty acid ester content prior to heating and contact with the catalyst. The catalyst may be, for example, a gallium-doped version of one or more zeolite- alumina matrix catalysts with pore sizes having 10 oxygen atoms in the pore mouth, such as ZSM-5, ZSM-11, ZSM-23, MCM-70, SSZ-44, SSZ-58, SSZ-35, and ZSM-22. Aromatics -production from the renewable oils is enhanced at higher gallium-cation levels, with the preferred level being about 1.0 Ga/framework-Al. While various renewable oils, or "bio-oils," may be used, algae oil has exhibited very high BTEX yields over the gallium cation catalyst, under conditions at or near 1 atm and approximately 400 degrees C.

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PRODUCTION OF AROMATICS FROM RENEWABLE RESOURCES

DESCRIPTION

[0001] This application claims priority of U.S. Provisional Application 61/427,160, filed December 24, 2010 and entitled "Production of Aromatics from Renewable Resources", the entire disclosure of which is incorporated herein by this reference.

BACKGROUND OF THE INVENTION

[0002] Field of the Invention

[0003] This invention relates generally to a method for the production of aromatics from renewable sources. More specifically, the preferred embodiments related to converting fat- or other lipid-containing oils derived from biomass, such as oil from naturally-occurring non-vascular photosynthetic organisms and/or from genetically modified non-vascular photosynthetic organisms; canola oil and other oils derived from vegetables such as corn, soybean, sunflower, and sorghum; and/or oils from other plant matter, seeds, fungi, bacteria, and other organisms both living and recently living.

[0004] Related Art

[0005] Aromatics, particularly benzene, toluene, ethylbenzene, and the xylenes (ortho, meta, and para isomers), which are commonly referred to as "BTEX" or more simply "BTX," are extremely useful chemicals in the petrochemical industry. They represent the building blocks for materials such as polystyrene, styrene-butadiene rubber, polyethylene terephthalate, polyester, phthalic anhydride, solvents, polyurethane, benzoic acid, and numerous other components. Conventionally, BTEX is obtained for the petrochemical industry by separation and processing of fossil-fuel petroleum fractions, for example, in catalytic reforming or cracking refinery process units, followed by BTX recovery units.

[0006] The patent literature describes refinery schemes proposed for processing biomass to produce transportation fuels, such as gasoline, jet, and diesel. See, for example, North Carolina State University, WO 2008/103204, published 28 August 2008, and entitled "Process for Convention of Biomass to Fuel". See also, Aravanis, et al., Publication US2009/0126260, published 21 May 2009, entitled "Methods of Refining Hydrocarbon feedstocks", and McCall, et al., Publication US2009/0158637, published 25 June 2009, and entitled "Production of Aviation Fuel from Biorenewable Feedstocks". The patent literature focuses, however, on transportation fuel production from renewable feedstocks, rather than aromatics production for the petrochemical industry. Also, the patent literature focuses on renewable feedstocks that are comprised mainly of triglycerides, for example, plant oils such as canola, soy bean, camelina and jatropha oils, and animal fats such as beef and lamb tallow and chicken fat, which are approximately 100% triglycerides.

[0007] There is a need for technology that produces high yields of aromatics from renewable sources. Particularly, there is a need for "green aromatics" that may be used, in place of petroleum-derived BTEX, in the petrochemical industry, for polymers, plastics, drugs, clothing, synthetic rubber, dyes, solvents, and other consumer and industrial products. There is a need for such "green aromatics" from algae oils, which have compositions much more complex than high-triglyceride plant oils and animal fats.

SUMMARY OF THE INVENTION

[0008] The invention comprises methods, catalyst, and/or equipment for converting one or more renewable oils to aromatics, for example, for use in the petrochemical industry and/or for blending components or additives for fuels. The invented processing methods comprise contacting one or more renewable oils with a catalytically-active form of gallium, for example, a catalyst comprising a catalytically-active form of gallium (also called "gallium-modified" catalyst herein). Such gallium-modified catalyst may comprise a zeolite or other solid that retains gallium in a catalytically-active form, for example, as gallium cations. The invention may comprise products made by said methods.

[0009] Said one or more renewable oils may be obtained from biomass, which is defined as a mass, or a material including a substantial amount of said mass, that is alive or that has been alive within the last 50 years. Examples of such renewable oils are canola oil and other lipids-based bio-oils derived from vegetables such as corn, soybean, sunflower, and sorghum; oil from naturally-occurring non-vascular photosynthetic organisms and/or from genetically modified non-vascular photosynthetic organisms, and/or oil from other plant matter, seeds, fungi, bacteria, and other organisms. The bio-oils may be extracted from their respective biomass by conventional techniques. As used herein, the term non-vascular photosynthetic organism includes, but is not limited to, macroalgae, microalgae and cyanobacteria (blue-green algae).

[0010] In certain embodiments, said one or more renewable oils feature a H/C mole ratio of greater than 1.5 (typically 1.7 - 2.1), and oxygen content of about 1 to about 35 wt-% (typically 5 – 15 wt%). The renewable oil(s) comprise large amounts of fatty acids or fatty acid esters, including free fatty acids and/or glycerol esters of fatty acids such as monoglycerides, diglycerides, and/or triglycerides. The H/C mole ratio, oxygen content, and relative amounts of free fatty acids and glycerol esters in said one or more renewable oils may depend on the source of the renewable oil and/or on the techniques of extraction from the biomass and/or pre-processing prior to contact with the gallium-modified catalyst, for example. The fatty acid moieties may range, for example, from about 4 to about 30 carbon atoms, but typically 10 to 25 carbon atoms, and even more typically, 16 to 22 carbon atoms. Most commonly, the fatty acid moieties are saturated or contain 1, 2 or 3 double bonds. Certain embodiments of the renewable oil(s) contain at least some triglycerides that are glycerol esters of C16 – C22 carboxylic acids and therefore may comprise C50+ compounds, however, many of the diglycerides and/or triglycerides in the renewable oil(s) decompose to their C-16 – C-22 components upon heating to elevated temperature. The renewable oil(s) may also comprise other materials such as carotenoids, hydrocarbons, phosphatides, simple fatty acids and their esters, terpenes, sterols, fatty alcohols, tocopherols, polyisoprene, carbohydrates and/or proteins.

[0011] Because of the high hydrogen to carbon ratio of certain embodiments of the renewable oil(s), and the dehydrogenation function of certain gallium-modified catalysts, some embodiments of the invention are expected to produce large amounts of hydrogen, and this hydrogen may be fed to hydrogen-consuming units in the refinery, for example, a hydrotreater or hydrocracker. Thus, some embodiments of the invention may be used both for "green" BTEX production and for "green" hydrogen production.

[0012] In certain embodiments, the gallium-retaining solid is a shape-selective material, and more typically, the solid is a zeolitic material wherein at least some of the cation-exchange centers are populated with gallium. In certain embodiments, the gallium-retaining solid(s) is/are gallium-doped version(s) of one or more zeolite-alumina matrix catalysts with pore sizes having 10 oxygen atoms in the pore mouth, for example, ZSM-5, ZSM-11, ZSM-23, MCM-70, SSZ-44, SSZ-58, SSZ-35, and ZSM-22. The inventors have discovered that aromatics-production from the renewable oils is enhanced at higher gallium levels, with one level being Ga occupying at least 90% of the cation sites and the protons or other cations previously at those cation sites having been replaced by Ga. An exemplary gallium level is 90 – 100% of the cation sites being replaced by Ga, which is called "1.0 Ga/framework-Al" herein.

[0013] Catalysts in certain embodiments of the invention may have gallium loadings above 1.0 Ga/framework-Al, that is, gallium present in an amount above that equal to 100% cation replacement. In such cases, extraframework Ga would exist, that is, Ga over and above the amount corresponding to 1 Ga/framework-Al and residing in zeolitic pores or on the exterior of the zeolite crystalline particles.

[0014] Although silica-alumina forms of zeolites are commonly used, zeolite frameworks may contain other metals, for example, gallium, boron, iron, phosphorous, germanium, indium, etc. Zeolite frameworks containing other metals may be suitable for producing gallium-modified catalyst, for example, for loading with gallium in cationic form for use as catalysts in certain embodiments of the invention.

[0015] The solid may be adapted to retain gallium by processes known to those of skill in the catalyst arts, for example, incipient wetness impregnation of zeolite with a gallium-composition dissolved in water. Methods for producing gallium-doped catalyst are also described in U.S. Patents No.4,727,206, 4,746,763, 4,761,511, and 5,149,679, the teachings of which are incorporated herein by this reference.

[0016] Said one or more renewable oils may comprise "whole crude oil", that is, the entire oil extract from biomass, and/or one or more fractions of said whole crude oil. Said one or more renewable oils may comprise whole crude oil(s)/fraction(s) that have been pre-processed before being fed to the gallium-catalyst process. For example, “pre-processing” in this context may include degumming, RBD (Refining, Bleaching, and Deodorizing, which is known in the art), thermal processing, hydrotreating, and/or other processes that deoxygenate or otherwise upgrade the renewable oil to some extent before being fed to the process comprising use of gallium-modified catalyst. Also, in certain embodiments, said one or more renewable oils may be co-processed (“co-fed”) with other oils, such as fossil petroleum oils/fractions, to the aromatics-production processes of this invention.

[0017] The inventors believe that many embodiments of the invention may be performed in conventional refining process equipment, that is, existing units or revamped existing units previously used entirely for fossil petroleum, or new units based on fossil petroleum technology but purpose-built to be optimized for renewable oil. Contacting said one or more renewable oils may be done in various flowschemes and refinery equipment, including but not limited to, a single reactor or series-flow reactors with optional removal of the liquid-phase from between the reactors prior to gas-phase flow to the downstream reactor(s); fixed or “packed” catalyst bed(s); fluidized catalyst bed(s); and/or moving bed(s). For example, said existing, revamped, or new units for certain embodiments of the invention may include those that are the same or similar to fluidized catalytic cracking (FCC) units (for example, see Figure 23), UOP CCR™ Cyclar™ units (for example, see Figure 24) , a UOP CCR Platformer™, naphtha reformer fixed-bed reactor(s), or other fixed-bed reactor units, all of which originated as fossil petroleum technology. Said FCC units have been designed for gasoline component production from petroleum, including those FCC units that minimize benzene production relative to higher octane components in order to maximize octane. Said UOP CCR™ Cyclar™ units are moving-catalyst, continuous-catalyst-regeneration units designed for aromatics production from petroleum C3 and C4 feeds using gallium catalysts. Said UOP CCR™ Platformer™ units are moving-catalyst, continuous-catalyst-regeneration units designed for high-octane gasoline production from petroleum naphtha, and typically use platinum catalysts to produce aromatics-rich liquid product. Said fixed-bed reactor units are also well known in the refinery arts, for example, “semi-regen” reformers that are designed for gasoline component production from petroleum naphtha, and typically use platinum or rhenium catalysts to produce aromatics-rich liquid product.

[0018] Feeding high percentages of renewable oils to process units based on fossil petroleum technology may require adaptation of equipment and operation upstream of the reactor(s)/riser(s) reaction zone, as none of the above-mentioned fossil petroleum units are designed specifically for said renewable oil feedstocks. The equipment and operation downstream of the reaction zone in these units, however, are more likely to effectively handle product streams from a high-percentage renewable oil(s) operation, due to the BTEX product from such embodiments being generally similar to the aromatics-rich products of the above-mentioned units. One possible exception is that modifications may be required in the equipment or operations downstream of the reaction zone to handle H2O, CO, and/or CO resulting from the high oxygen content of certain renewable oils. Alternatively or in addition, pre-processing for deoxygenation of renewable oils, prior to being fed to said reaction zone, may prevent excessive water production and hydrogen consumption in said reaction zone.

[0019] Feeding low-percentages of renewable oils to process units based on fossil petroleum technology may be a desirable option, especially because said one or more renewable oils are expected to be available only in relatively small quantities in the next few years. Therefore, co-processing of said one or more renewable oils with other feedstocks may be required and/or beneficial, resulting in process units that are "fed-in-part" with said one or more renewable oils, and "loaded-in-part" with gallium-modified catalyst. While "fed in full" means herein that about 100 wt% (for example, 99 – 100 wt%) of the feedstock for a process unit would be said one or more renewable oils, the term "fed-in-part" means herein that a lesser percentage of the feedstock would be said one or more renewable oils. While "loaded-in-full" means herein that about 100 wt% (for example, 99 – 100 wt%) of the catalyst for a process unit would be gallium-modified catalyst (for example, gallium-cation catalyst), the term "loaded-in-part" means that a lesser percentage would be gallium-modified catalyst.

[0020] Optimum operating conditions, including conditions of feedstock contact with catalyst, for such loaded-in-part and fed-in-part operations may be different from those suggested by the loaded-in-full and fed-in-full Examples later in this document. For example, higher temperatures for higher space velocities or fluidized bed or moving bed conditions may be needed. In such cases, optimum feedstock-catalyst-contact temperature may be as high as 600°C, but more typically may be in the 450 – 550°C range, for example. Based on the data disclosed herein and data available to refiners from fossil petroleum operations, those of skill in the art may optimize the conditions of such loaded-in-part and fed-in-part operations without undue experimentation.

[0021] In certain embodiments, said one or more renewable oil(s) may be pre-processed prior to being fed or co-fed to a unit containing at least some gallium-modified catalyst. For example, pre-processing steps may comprise thermal-treatment and/or hydrotreatment of the renewable oil(s) or fractions thereof. For example, a processing scheme comprising hydrotreatment, or thermal-treatment followed by hydrotreatment, of algae oil, is expected to produce a desirable feed or co-feed for an FCC unit. Alternatively, a processing scheme comprising thermal-treatment of a portion of algae oil, for example, a heavy fraction of algae oil, followed by hydrotreatment of both the thermally-treated and non-thermally-treated fractions of the renewable oil, may also produce a desirable feed or co-feed for an FCC unit.

[0022] Embodiments of the invention are not necessarily limited to the above-mentioned units or co-processing options. Other processing units, flowschemes and/or other co-feedstocks may provide synergistic or beneficial results.

BRIEF DESCRIPTION OF THE DRAWINGS

[0023] Figure 1A is a schematic of the laboratory reactor system, using a single reactor, used in the experiments of Examples I, III, and IV,

[0024] Figure 1B is a schematic of the laboratory reactor system, used in the experiments of Example II, that includes two reactors in series and is adapted for liquid product removal between reactors.

[0025] Figure 2 is a graph of weight-percent yield of liquid products (triangles) and vapor products (squares) from Runs SAP275-279 on HZSM-5 catalyst (no gallium) in Example I, showing that increasing temperature decreases the yield of liquid products while increasing the amount of vapor products.

[0026] Figure 3 is a graph of vapor product yields changing with increasing amounts of gallium (left to right) added to the catalyst for experiments SAP281-283 in Example I, showing particularly that propane and ethane changed with increasing gallium. Molecules shown in this graph represent ~98% of all vapor products from each experiment. Results for 0.0 Ga are the mean of SAP284-287 and the “error bars” show the 95% confidence interval.

[0027] Figure 4 is a graph of yields of liquid product (triangles), vapor product (squares), and coke on catalyst (circles) vs. increasing gallium-loading of the catalyst in experiments SAP281-283 of Example I. With increasing gallium content, liquid yield (triangles) increased, coke (circles) stayed almost constant, and vapor products (squares) decreased. The mean of SAP284-287 (no Ga) is used in this graph for zero gallium content.

[0028] Figure 5 is a graph of boiling point distribution of the organic phase products, for the various gallium loadings (increasing left to right) in Example I. The majority of the products fall in the 60-188°C range.

[0029] Figure 6 is a graph of benzene, toluene, ethyl-benzene, xylene, and total BTEX yields, in Example I, showing that BTEX yield increases with the gallium content of the ZSM-5 catalyst.

[0030] Figure 7 is a graph of vapor product yields obtained from algae oil cracking at 400°C, over GaZSM-5 (bars on left) and HZSM-5 catalyst (bars on right) in Example III.

[0031] Figure 8 is a graph of yields of individual BTEX components, total BTEX, and gasoline obtained from algae oil cracking over catalysts at 400°C, over GaZSM-5 catalyst (bars on left) and HZSM-5 catalyst (bars on right) in Example III.

[0032] Figure 9 is a graph of gas phase products produced during cracking of gas oil in Example IV.

[0033] Figure 10 is a graph of the BTEX and gasoline yield results from cracking of gas oil (Example IV) compared to BTEX and gasoline yield results from cracking of algae oil (Example III), both at 400 degrees C.

[0034] Figure 11 is a graph of the simulated distillation curve of the Conoco Phillips gas oil of Example IV compared to the simulated distillation curve of algae oil of Example III, with a maximum gasoline boiling point line included for reference.

[0035] Figure 12 is a graph of the simulated distillations for the gas oil product (Example IV), algae oil product (Example III) and canola oil product (Example I) for the respective cracking experiments.

[0036] Figure 13 is a graph of conversion % vs. catalyst/oil ratio for the algae oil feed and vacuum gas oil samples of Example V.

[0037] Figure 14 is a graph of coke wt % vs. conversion ratio for the algae oil feed and vacuum gas oil samples of Example V.

[0038] Figure 15 is a graph of conversion % vs. catalyst/oil ratio for algae oil feed, hydrotreated algae oils, and vacuum gas oil, in Example VI. Note that this graph comprises the hydrotreated algae oil data added to the algae oil feed and vacuum gas oil data of Figure 13.

[0039] Figure 16 is a graph of coke wt % vs. conversion for algae oil feed, hydrotreated algae oils, and vacuum gas oil, in Example VI. Note that this graph comprises the hydrotreated algae oil data added to the algae oil feed and vacuum gas oil data of Figure 14.

[0040] Figures 17 – 22 are graphs of the wt % yields of gasoline, LCO, DCO, TC2, TC3, and TC4, respectively, versus conversion %, for the algae oil feed, hydrotreated algae oils, and vacuum gas oil of Example VI.

[0041] Figure 23 is a schematic illustration of one example of a conventional fluidized catalyst conversion unit (FCC), which may be adapted to operate in certain embodiments of the invention.

[0042] Figure 24 is a schematic illustration of one example of a conventional UOP CCR™ Cyclar™ unit, which may be adapted to operate in certain embodiments of the invention.

DETAILED DESCRIPTION

[0043] Referring to the following detailed description, including Examples I – IX, and the associated tables and figures, there are described several, but not the only, embodiments of the invented methods, equipment, and products.

[0044] The inventors believe that the data from the laboratory-scale experiments of Examples I – VII are roughly predictive of what would happen in commercial units. For example, the data in Examples I – III would be roughly predictive of an operation having packed bed gallium-cation catalyst loaded-in-full, renewable oil(s) fed-in-full (including canola oil and algae oil), the feed-catalyst contact at about 1.0 WHSV (weight hourly space velocity), and the temperature controlled in the range of 350 - 450 degrees C, for example, 400 degrees C. The data in Example IV would be roughly predictive of a fossil petroleum gas oil feed processed over the selected gallium-modified catalyst and conditions from Example I and III, and, hence, that Example IV may be used to predict performance differences between the renewable oils and the gas oil. The data in Examples V and VI would be roughly predictive of

FCC processing of algae oil and hydrotreated algae oil, respectively. The data in Example VII would be roughly predictive of thermal treatment of certain algae oils, as a pre-processing step prior to subsequent upgrading by hydrotreating and fluid catalytic cracking with gallium-modified catalyst.

[0045] The experimental data of Examples I – III support certain embodiments wherein renewable oil are processed effectively over gallium-modified catalyst while achieving very beneficial results in aromatics and hydrogen production, wherein optionally gas oil may also be effectively processed over the same gallium-modified catalyst (Example IV). The combination of the gallium-cation catalyst data in Examples I – IV and the FCC data in Examples V and VI supports certain embodiments of the invention wherein algae oils are upgraded by a pre-processing step of hydrotreating, followed by fluid catalytic cracking (optionally with petroleum as a co-feed), wherein the FCC catalyst comprises supplemental gallium-cation catalyst to further enhance aromatics production from the algae oil in said fluid catalytic cracking. The combination of the gallium-catalyst data in Examples I – IV, the FCC data in Examples V and VI, and the thermal treatment data of Example VII supports certain embodiments of the invention wherein algae oils are upgraded by pre-processing steps of thermal treatment and hydrotreating, followed by FCC fluid catalytic cracking (optionally with petroleum as a co-feed), wherein the FCC catalyst comprises supplemental gallium-cation catalyst to further enhance aromatics production from the algae oil in said fluid catalytic cracking.

[0046] In certain embodiments, one or more renewable oils will be co-fed (or “fed-in-part”) with other oils wherein the combined feed contacts a gallium-modified catalyst. The broad scope of the invention may comprise processing any amount of any renewable oil, including those obtained from biomass by solvent extraction, by the HTT techniques above, or other biomass treatment/extraction techniques and fractions thereof, in a operation with gallium-modified catalyst, with the renewable oil being any percentage of the total feedstock. For example, one or more renewable oils may constitute as little as about 1 wt% of the feedstock to a unit containing the gallium-cation-retaining catalyst, but due to the large BTEX benefit exhibited by the catalyst with renewable oil(s), the inventors anticipate that the renewable oil(s) will eventually constitute a major portion of the total feedstock of selected process units; for example, at least 5 wt%, at least 10 wt%, at least 50 wt-%, or at least 80 or 90 wt-% of the total feedstock to the process unit will be said one or more renewable oil in certain embodiments. Therefore, in such embodiments, the renewable oil will be in the range of 5 – 100 wt%, 10 – 100 wt%, 50 – 100 wt-% of the feedstock, 80 – 100 wt% or 90 – 100 wt% of the feedstock to one or more selected units. In some embodiments, components for blending with said one or more renewable oils prior to processing over gallium-modified catalyst may be selected from the group consisting of: fossil fuel, petroleum, C3 – C4, naphtha, gasoline, jet fuel, diesel, gas oil, heavy gas oil, and any combination thereof. In co-processing in an FCC unit, it is expected that renewable oil(s) may be co-processed with gas oil/vacuum gas oil, for example. In co-processing in a Cyclar™ unit, it is expected that renewable oil(s) may be co-processed with C3 – C4, for example.

[0047] Certain of the feed-co-processing embodiments also comprise the gallium-modified catalyst being loaded/charged with other catalysts into the unit (a "loaded-in-part" operation), for example, with non-gallium-containing catalysts. The gallium-modified catalyst may constitute any percentage of the catalyst load/stream. For example, the gallium-modified catalyst may constitute as little as about 1 wt% of the catalyst in the process unit, but, due to the large BTEX benefit exhibited by the catalyst with renewable oil(s), the inventors anticipate that the catalyst will eventually constitute at least 5 wt%, at least 10 wt%, at least 50 wt%, at least 80 wt%, or at least 90 wt% of the total catalyst in the unit. Therefore, in such embodiments, the gallium-modified catalyst will be in the range of 5 – 100 wt %, 10- 100 wt%, 50 – 100 wt%, 80 – 100 wt%, or 90 – 100 wt% of the total catalyst. It should be noted that the term "gallium-modified catalyst" herein and in the claims is broadly defined as any solid comprising a catalytically-active form of gallium, which may include but is not necessarily limited to gallium-cation catalyst, gallium-doped zeolites, and the other examples of gallium-modified catalysts in this document.

[0048] For example, in a fluid catalytic cracking unit, it is expected that renewable oil(s) could be fed-in-part to the FCC unit, along with gas oils or other petroleum feedstocks. In such embodiments, only a portion of the total feedstock fed to the FCC process unit would be renewable oil(s), for example, less than 99 wt% and more likely 1 - 20 wt% or 5 – 10 wt% of the total feedstock. In such embodiments, it is expected that gallium-cation catalyst would be an additive/supplement to the catalyst stream of the FCC units, which normally consists essentially of acidic zeolite FCC catalyst such as zeolite Y catalyst. In such embodiments, only a portion of the total catalyst loading/charge (stream) would be gallium-modified catalyst, for example, less than 99 wt% and more likely 1 - 20 wt% or 5 - 10 wt% of the total catalyst load/stream. The FCC catalyst and gallium-cation catalyst would be regenerated together in the regenerator section of the FCC unit. Reaction temperature may be adjusted in such scenarios, to optimize overall performance based on the mix of catalyst and feeds in the unit, and would be expected to be in the range of about 400 – 555 degrees C, ,for example.

[0049] Catalyst supplementation or change-out would not necessarily be required in order to feed said one or more renewable oils to a UOP Cyclar™ unit, as such units have typically used gallium-cation catalysts for conversion of C3 and C4 feedstock. Likewise, catalyst regeneration in a Cyclar ™ unit would be expected to be effective, as the Cyclar ™ CCR™ regeneration section is designed for gallium-cation catalysts that are similar to those of certain embodiments of the invention. Therefore, due to existing Cyclar™ units being loaded with and adapted for gallium catalyst, it may be possible to feed renewable oil(s) in-full, or in-part along with C3 and C4 feeds or other feeds, to Cyclar™ or similar units.

[0050] While UOP CCR Platformers™ or fixed-bed naphtha reformer reactor(s) may be candidate units for certain embodiments of the invention, it may be noted that gallium-cation catalysts are not expected to require the relatively complex regeneration process required for the platinum reforming catalysts typically used in Platformers™ and many other naphtha reformers. Certain gallium-cation catalysts may be regenerated by a coke burning step, followed by reduction during processing of oil over the catalyst, that is, at the temperature and in the environment in which the renewable oil is being processed over the catalyst. Therefore, an oxidation-only regeneration section such as in an FCC unit, or a simple batch oxidization, may be effective for regeneration of certain catalysts of the invention, rather than oxygenation followed by a special reduction process and equipment such as is used in a UOP CCR Platformer™. In certain embodiments provided in a fixed-bed catalytic reformer, it is expected that one of the series-flow reactors would be loaded with the gallium-cation catalyst, for example, with the other reactors being loaded with conventional reforming catalyst, and with adaptation for separate regeneration of the reactors and, hence, of the multiple types of catalyst.

[0051] The protonated form of the zeolite/alumina matrix catalyst used in Examples I – IV may be described as the simplest form of the zeolite/alumina matrix catalyst, wherein the cation-exchange centers in the zeolite are fully populated with protons. Each cation center is associated with an aluminum atom incorporated in the framework of the zeolite. Therefore, one may say that the proton to framework-Al ratio of the protonated form is 1/1, and the form is called “HZSM-5” (the “H” or more strictly “H^+” being a proton), wherein ZSM-5 stands for “ Zeolite Socony Mobil – 5” (structure type MFI – mordenite framework inverted).

[0052] The gallium-loaded forms of the zeolite/alumina matrix catalyst used in Examples I – IV were prepared with gallium levels that are cited as a fraction of the cation sites replaced by gallium. Catalysts were prepared with Ga levels equivalent to 1.0 Ga/framework-Al, 0.33 Ga/framework-Al, and 0.10 Ga/framework-Al. In these materials, Ga replaced protons. Therefore, for 1.0 Ga/framework, almost all the cation sites were occupied by Ga and almost all the protons had been replaced by Ga. Therefore, the “1.0 Ga/framework-Al” catalyst may be described as having 90% - 100% of cation sites occupied by Ga or 95 – 100% of cation sites occupied by Ga. For the other Ga loadings, only a portion of the protons had been replaced with Ga. In some tables, the term “0 Ga/framework-Al” is used, which means zero protons replaced by Ga and which may be equivalently be referred to as “HZSM-5” (or the “fully protonated form” of the catalyst). Exemplary catalysts have gallium as cations, which compensate for the anionic framework of the zeolite. It may be noted that, many embodiments of the catalysts of this invention are not acidic-type zeolites comprising gallium instead of aluminum in the framework.

[0053] Gallium catalysts have been described for producing aromatics from short-chain fossil-fuel hydrocarbons, especially C2, C3, and C4. U.S. Patent No. 4,727,206 discloses gallium catalyst for feedstocks having methane as a major component, with ethane and C3 – C6 optionally being included in the feedstock. U.S. Patent No. 4,746,763 discloses gallium catalyst for processing of C2 – C6 aliphatic compounds. U.S. Patent No. 4,761,511 describes catalysts for aromatics production and suggests that C2 – C12 paraffins may be used as feedstock, but the patent teaches that C2 – C8 paraffins are the preferred feedstock, and that C2 – C4 paraffins are the especially preferred feedstock. U.S. Patent No. 4,766,265 discloses liquid aromatic production from ethane (C2). U.S. Patent No. 4,855,522 mentions gallium catalyst for processing C2 – C12 compounds, but focuses on C5 – C7 paraffin feedstocks. U.S. Patent No. 5,149,679 mentions C2 – C12 feedstocks, but prefers C2 – C6, and especially prefers C2 – C4 feedstocks.. UOP Cyclar™ units have utilized some of the catalysts mentioned in these patents with C3 and C4 feedstocks. Thus, gallium-cation catalysts are known, and those of skill in the catalytic arts will understand how to make such catalysts.

[0054] The inventors believe, however, that the prior art teaches away from applying such gallium catalysts to aromatics production and/or hydrogen production from renewable oils, especially those with substantial C12+ compounds, substantial C16 – C22 fatty acid/ester chains, and/or even substantial C50+ compounds. It is not obvious to apply such gallium catalysts to renewable oils that comprise biological compounds which contain oxygen, such as fatty acids, triglycerides, aldehydes, ketones, esters, and/or alcohols, etc. that occur in significant amounts in naturally-occurring plant oils. The inventors believe that it is surprising and non-obvious to apply such gallium catalysts, which have been designed for and applied to C2-C4 feedstocks, to BTEX production and/or hydrogen production from renewable oils, and, particularly, from canola oil or algae oil.

[0055] The renewable crude oils of this disclosure may be extracted by various means from biomass that has been alive within the last 50 years. As an example, the canola oil used in the experiments of Examples I and II was commercially-available canola oil, which is a well-known oil obtained from rapeseed. As another example, the renewable algae oils used in the experiments of Examples III – V were examples of the category of renewable oils that may be extracted by various means from of naturally-occurring non-vascular photosynthetic organisms and/or from genetically-modified non-vascular photosynthetic organisms. Genetically modified non-vascular photosynthetic organisms can be, for example, where the chloroplast and/or nuclear genome of an algae is transformed with a gene(s) of interest. As used herein, the term non-vascular photosynthetic organism includes, but is not limited to, algae, which may be macroalgae and/or microalgae. The term microalgae includes, for example, microalgae (such as *Nannochloropsis* sp.), cyanobacteria (blue-green algae), diatoms, and dinoflaggellates. Crude algae oil may be obtained from said naturally-occurring or genetically-modified algae wherein growing conditions (for example, nutrient levels, light, or the salinity of the media) are controlled or altered to obtain a desired phenotype, or to obtain a certain lipid composition or lipid panel.

[0056] In certain embodiments, the biomass is substantially algae, for example, over 80 wt% algae, or over 90 wt % algae, or 95 – 100 wt% algae (dry weight). Algae biomass of particular interest comprises photosynthetic algae grown in light. Other embodiments, however, may comprise obtaining algae biomass or other "host organisms" that are grown in the absence of light. For example, in some instances, the host organisms may be photosynthetic organisms grown in the dark or organisms that are genetically modified in such a way that the organisms' photosynthetic capability is diminished or destroyed. In such growth conditions, where a host organism is not capable of photosynthesis (e.g., because of the absence of light and/or genetic modification), typically, the organism will be provided with the necessary nutrients to support growth in the absence of photosynthesis. For example, a culture medium in (or on) which an organism is grown, may be supplemented with any required nutrient, including an organic carbon source, nitrogen source, phosphorous source, vitamins, metals, lipids, nucleic acids, micronutrients, and/or an organism-specific requirement. Organic carbon sources include any source of carbon which the host organism is able to metabolize including, but not limited to, acetate, simple carbohydrates (e.g., glucose, sucrose, and lactose), complex carbohydrates (e.g., starch and glycogen), proteins, and lipids. Not all organisms will be able to sufficiently metabolize a particular nutrient and that nutrient mixtures may need to be modified from one organism to another in order to provide the appropriate nutrient mix. One of skill in the art would know how to determine the appropriate nutrient mix.

[0057] In certain embodiments, algae from which suitable oil may be extracted are *Chlamydomonas sp. for example Chlamydomonas reinhardtii.*, *Dunaliella sp., Scenedesmus sp., Desmodesmus sp., Chlorella sp., and Nannochloropsis sp.* Examples of cyanobacteria from which suitable crude oil may be obtained include *Synechococcus* sp., *Spirulina sp., Synechocystis* sp. *Athrospira* sp., *Prochlorococcus* sp., *Chroococcus* sp., *Gleoecapsa* sp., *Aphanocapsa* sp., *Aphanothece* sp., *Merismopedia* sp., *Microcystis* sp., *Coelosphaerium* sp., *Prochlorothrix* sp., *Oscillatoria* sp., *Trichodesmium* sp., *Microcoleus* sp., *Chroococcidiopisis* sp., *Anabaena* sp., *Aphanizomenon* sp., *Cylindrospermopsis* sp., *Cylindrospermum* sp., *Tolypothrix* sp., *Leptolyngbya sp., Lyngbya sp.,* or *Scytonema* sp..

[0058] Algae production and extraction technology are known in the art, including genetically-modified algae growth and extraction, and certain embodiments of the invention comprise crude algae oil feedstocks/fractions from any growth and extraction techniques. Algae may be harvested and dried and then the oil extracted from lysed or destroyed cells. The cells may be chemically lysed, or mechanical force can be used to destroy cell walls. Oil may be extracted from the lysed/destroyed cells using an organic solvent such as hexane. The algae oil used in Example III was oil extracted from algae biomass using hexane, and then treated by a conventional RBD process, such as that known in the food arts for vegetable oils. The algae oil if Example III was not hydrotreated, reformed, or cracked prior to being processed in the zeolitic catalyst cracking processes.

[0059] Alternative Techniques of Obtaining Crude Algae Oil from Biomass

[0060] Certain embodiments comprise crude algae oils that are obtained by techniques comprising steps other than or in addition to solvent extraction. For example, certain embodiments comprise hydrothermal treatment of the biomass prior to solvent extraction of the crude algae oil, for example, by heptanes, hexanes, and/or MIB, and then processing by embodiments of the invention without RBD treatment. Certain algae oil feedstocks, therefore, have not been subjected to any RBD processing (the refining, bleaching, and deodorizing process conventionally known and used for high-triglyceride bio-oils), nor subjected to any of the individual steps of refining, bleaching or deodorizing, after being extracted and before certain upgrading processes of the invention.

[0061] Certain embodiments of said hydrothermal treatment comprise an acidification step. Certain embodiments of the hydrothermal treatment comprise heating (for clarity, here, also called “heating to a first temperature”), cooling, and acidifying the biomass, followed by re-heating and solvent addition, separation of an organic phase and an aqueous phase, and removal of solvent from the organic phase to obtain an oleaginous composition. A pretreatment step optionally may be added prior to the step of heating to the first temperature, wherein the pretreatment step may comprise heating the biomass (typically the biomass and water composition of step (a) below) to a pretreatment temperature (or pretreatment temperature range) that is lower than said first temperature, and holding at about the pretreatment temperature range for a period of time. The first temperature will typically be in a range of between about 250 degrees C and about 360 degrees, as illustrated by step (b) listed below, and the pretreatment temperature will typically be in the range of between about 80 degrees C and about 220 degrees C. In certain embodiments the holding time at the pretreatment temperature range may be between about 5 minutes and about 60 minutes. In certain embodiments, acid may be added during the pretreatment step, for example, to reach a biomass-water composition pH in the range of about 3 to about 6. It should be noted that the hydrothermal-treatment and solvent-extraction methods may be conducted as a batch, continuous, or combined process.

[0062] Certain embodiments of the hydrothermal-treatment and solvent-extraction procedures (HTT) may comprise:

a) Obtaining an aqueous composition comprising said biomass and water;
b) Heating the aqueous composition in a closed reaction vessel to a first temperature between about 250 degrees C and about 360 degrees C and holding at said first temperature for a time between 0 and 60 minutes;
c) Cooling the aqueous composition of (b) to a temperature between ambient temperature and about 150 degrees C;
d) Acidifying the cooled aqueous composition of (c) to a pH from about 3.0 to less than 6.0 to produce an acidified composition;
e) Heating the acidified composition of (d) to a second temperature of between about 50 degrees C and about 150 degrees C and holding the acidified composition at said second temperature for between about 0 and about 30 minutes;
f) Adding to the acidified composition of (e) a volume of a solvent approximately equal in volume to the water in said acidified composition to produce a solvent extraction composition, wherein said solvent is sparingly soluble in water, but oleaginous compounds are at least substantially soluble in said solvent;
g) Heating the solvent extraction composition in closed reaction vessel to a third temperature of between about 60 degrees C and about 150 degrees C and holding at said third temperature for a period of between about 15 minutes and about 45 minutes;
h) Separating the solvent extraction composition into at least an organic phase and an aqueous phase;
i) Removing the organic phase from said aqueous phase; and
j) Removing the solvent from the organic phase to obtain an oleaginous composition.

[0063] The composition of crude algae oils obtained by the above hydrothermal-treatment and solvent-extraction techniques ("HTT crude algae oils") may differ from the composition of solvent-extracted and RBD-treated algae oils such as that in Example III, and certain embodiments of the invention may comprise said one or more renewable oils comprising, consisting essentially of, or consisting of said HTT crude algae oils or fractions thereof.

[0064] The following Examples illustrate certain embodiments of the methods described herein, wherein a substantially higher yield of BTEX is achieved by contact with gallium-modified catalyst compared to non-gallium-modified catalyst. The Examples illustrate and enable embodiments of the invention, but the invented methods, apparatus, and/or catalyst are not necessarily limited to the details therein, for example, algae oils other than those of the Examples are included in the broad scope of the invention. Also, various reactor and product recovery configurations, gallium-retaining catalyst compositions, catalyst-to-oil ratios, catalyst-feedstock contact time, feedstock conversions, temperatures, and pressures, including others than those detailed in the Examples, are included in the broad scope of the invention. Those of skill in the art of refining operations, after reading and viewing this disclosure, will understand how to apply the described technology to commercial refining operations to achieve substantial benefits such as are illustrated herein.

EXAMPLES

[0065] Example Summary

[0066] Examples I – III detail processing of canola oil or algae oil in multiple tests using zeolite-alumina matrix catalysts, including catalyst in protonated form and in gallium-cation-retaining form. The tests showed excellent yields of BTEX from both canola oil and algae oil, especially when the gallium-form was used, and may be indicative of the BTEX yields and/or yields trends that may be achieved with certain other renewable oils, including those from other plant, non-vascular photosynthetic organism, vegetable, seed, fungi, and bacteria sources.

[0067] Example IV details processing of fossil petroleum gas oil over a selected gallium-cation-retaining catalyst from Examples I – III, for comparison to the results from the renewable oil processing.

[0068] Examples V and VI detail processing of algae oil and hydrotreated algae oil by fluid catalytic cracking, compared to fossil petroleum vacuum gas oil, and describe certain embodiments wherein the FCC catalyst is supplemented with gallium-modified catalyst.

[0069] Example VII describes processing of algae oil by thermal treatment, followed by hydrotreatment and fluid catalytic cracking, and describes certain embodiments wherein the FCC catalyst is supplemented with gallium-modified catalyst.

[0070] Example VIII describes an exemplary FCC process unit commercial application, including structure details of the fluidized bed and systems for making-up/supplementing catalyst and additives to said fluidized bed.

[0071] Example IX describes an exemplary purpose-built process unit commercial application, which may be similar to a UOP Cyclar™ unit and is designed for a feedstock comprised substantially or entirely of renewable oil.

[0072] Analysis of Example Feeds

[0073] The canola oil of Examples I and II was a commercially-available oil obtained from rapeseed, containing approximately 60 - 70 wt-% C18:1 and approximately 12 wt% oxygen.

[0074] The algae oil of Example III was of the type analyzed in Tables 1 – 3 below. One may note the 48.8 wt-% free fatty acids, with 45.5 wt-% being C18:1 free fatty acids (carbon chain length = 18, monounsaturated). A portion of the free fatty acids in this algae oil may be those naturally-occurring in the algae and a portion may be fatty acids "freed" from their glyceride compounds during extraction from the algae. Note also the algae oil oxygen content of 10.52 wt%.

[0075] Table 1. Crude Algae Oil Analyses (weight-%)

% C	78.62
% H	11.47
% N	0.22
% O	10.52
S PPM	323.0
P PPM	17.0

[0076] Table 2. General Composition of Crude Algae Oil

Parameters	Crude Algae Oil (Bottles 1-4)
Elements by ICP	
P (ppm)	56
Fe (ppm)	19.7
Ca (ppm)	26.5
Mg (ppm)	4.3
Na (ppm)	12.7
K (ppm)	5.1
N (ppm)	1132
S (ppm)	493
Chlorophyll (ppm)	11654
FFA (% as C18:1)	45.5
Hexane insoluble impurities (%)	0.40
GC composition (%)	
Short chain undefined compounds	0.47
FFA / Fatty Alcohols	53.14
Monoglycerides	1.03
Diglycerides	1.13
Triglycerides	3.25
Tocopherols	1.32
Free Sterols	2.59
Waxy like compounds	9.09
Unknown / Not Detected	25.84
Tocopherols	
α-tocopherol	820
β-tocopherol	Traces
γ-tocopherol	Traces
δ-tocopherol	N.D.
Unsaps (%)	29.13

[0077] Table 3. General Analyzes of Crude Algae Oil

Analysis	Crude Algae Oil
Acid Value (mg KOH/g)	97.1
Free Fatty Acids (%)	48.8
Insoluble impurities (%)	0.01
Neutral Oil (%)	53.3
Chlorophyll in Oil (ppm)	5530
Carotenes Profile	
Astaxanthin (ppm)	143
Lutein (ppm)	1510
Zeaxanthin (ppm)	624
alpha-Carotene (ppm)	370
trans-beta Carotene (ppm)	2540
cis-beta Carotene (ppm)	2790
Lycopene (ppm)	<10
Total Carotenes (ppm)	7970
Phospholipids	
N-acylphosphatidylethanolamine (%)	<0.01
Phosphatidic Acid (%)	<0.01
Phosphatidylethanolamine (%)	<0.01
Phosphatidylcholine (%)	<0.01
Phosphatidylinositol (%)	<0.01
Lysophosphatidylcholine (%)	<0.01
Residual Solvents GC/MS	
Hexane (ppm)	16100
Cyclohexanone (ppm)	530
Methyl Benzene (est) (ppm)	˜500
Ethyl Benzene (est) (ppm)	˜400
Propyl Benzene (est) (ppm)	˜150
Chloroform (est) (ppm)	˜2.00
Sterols and Stanols (Free) (mg/g)	11.0
Tocopherols and Sterols	
Delta Tocopherol (mg/100g)	5.09
Gamma Tocopherol (mg/100g)	3.04
Alpha Tocopherol (mg/100g)	76.0
Cholesterol (mg/100g)	405
Campesterol (mg/100g)	34.2
Stigmasterol (mg/100g)	124
B-sitosterol (mg/100g)	780
Other Sterols (mg/100g)	733

[0078] The algae oil feed tested or referenced in Examples III - VI was obtained by the HTT steps a – j above and is described in Tables 4-6 below.

[0079] Table 4. % Mass Fraction – Algae Oil Feed

Sample	FRACTION MASS % Initial – 260 °F	260-400 °F	400-490°F	490-630°F	630-1020°F	1020° F
NS-263-061 Algae Oil Feed	0.0	0.5	1.3	6.6	64.1	27.5

[0080] Table 5. Compound Classes – Summary for Algae Oil Feed

Class	Algae Oil Feed
HC-Saturated	2.0
HC-Unsaturated	9.1
Naphthenes and Aromatics	1.7
N-Aromatics	8.6
Nitriles	0.0
Acid Amides	10.9
Fatty Acids	25.9
Oxygen Compounds	1.3
Sterols	13.6
Sulfur Compounds	0.0
Unknowns	26.9

[0081] Table 6. Elemental Analysis – Algae Oil Feed

wt %	Algae Oil Feed
C	77.9
H	10.7
N	3.9
O	6.8
S	0.37

[0082] Experimental Equipment Summary

[0083] Examples I and III used the 20 g scale reactor system 10 schematically portrayed in Figure 1A. The reactor system was controlled by a LabVIEW™ program and National Instruments DAQ hardware. For runs using canola oil, a dual piston chromatography pump 12 pulled reactant from a flask of feedstock 14, and pumped it up to a furnace 16 containing the reactor 18. For algae oil runs, the feed pump was an ISCO piston pump with 500 cc capacity which was able to handle the highly viscose algae oil. No feedstock preheat furnace 20 was used because it was determined previously that it was thermally cracking the canola oil before it could reach the catalyst. The reactant mixed with a heated nitrogen stream 22 just before entering the top of the reactor 18. The mixed nitrogen and reactant flowed down the reactor through the catalyst bed 24. Reactor effluents passed through a cooling coil 26 and a liquid trap 28, both contained in ice baths 30. The cooled vapor left the liquid trap and passed through a micro-GC 32 and then on to a vent. An Agilent 2804 micro-GC measured the composition of the vapor phase every 4 minutes.

[0084] The reactor 18 in Examples I and III was a ½ inch diameter stainless steel reactor tube, measured 24 inches long, and contained a 10 g catalyst bed 24 centered within the furnace's 18" heated zone. Glass beads 40 packed in the bottom of the reactor supported the catalyst bed and glass beads 42 above the bed helped to vaporize the feed before it reached the catalyst. In preliminary work, using a preheat furnace for the feedstock resulted in thermal cracking of the canola oil before it could reach the catalyst, and so the feedstock preheat furnace 20 was not used in the experiments in Examples I – III.

[0085] Two thermocouples inserted axially into the catalyst zone of the tubular reactor measured the temperature 2 inches below the top and 2 inches above the bottom of the catalyst bed in Examples I and III. Thermocouples also were mounted in the heated spaces of the furnace. A LabVIEW™-based control program adjusted the furnace temperature so that the average of the top and bottom catalyst temperatures stayed on setpoint. The same program also controlled the pump and gas flow controllers, while logging all temperatures and flowrates. The programmable Chromtech™ dual-piston pump supported flowrates from 0.001 to 12.00 mL min, although the viscosity of the canola oil limited the pump to flowrates of not more than around 1 mL/min without providing backpressure. The ISCO pump used to deliver algae oil was programmable to deliver from 0.001 to 204 cc/min of feed. A pair of Brooks Instruments mass flow controllers worked in tandem to accurately provide nitrogen flow rates up to 10 SLM. This one-reactor system and its use are further described below in Example I.

[0086] The mass of liquid product from each experiment of Examples I and III was measured, and then the organic phase was separated from the aqueous phase and the mass of the remaining aqueous phase was measured. When catalyst charges were removed from the reactor, a small sample was used in a microbalance system to estimate coke content, then the remainder of the used catalyst was placed in a horizontal tube furnace to be regenerated by burning in 80/20 Ar/O_2 at 575°C for 4 hours. The percent difference between the mass of the catalyst before and after regeneration was taken as the actual coke content, and this matched well with microbalance measurements of coke content. The total vapor product reported for each experiment represents an estimate based on the micro-GC measurements of the gaseous product composition over time. The composition data was integrated over time to yield a total amount of each gaseous product.

[0087] Example II used a reactor system modified, as shown schematically in Figure 1B, to include two reactors in series with liquid removal between the two reactors. Each of the two reactor structures, reactor loading, temperature control, product condensation, and product stream measurement and analysis for Example II were substantially the same as the equipment and methods described above for the single-reactor Examples I and III. The two-reactor system and its use are further described below within Example II.

[0088] Example IV utilized equipment and procedures that were substantially similar or the same as those used in Examples I and III, as will be understood from reading Example IV. Example V utilized equipment and procedures for FCC MAT testing, and Example VI utilized equipment and procedures for hydrotreating followed by FCC MAT testing, as will be understood from reading these examples, respectively.

Example I: Catalytic cracking of Canola Oil over GaZSM-5

[0089] Catalytic cracking of canola oil was conducted over a gallium-doped HZSM-5 zeolite catalyst, hereafter called “GaZSM-5”, in a 20 g scale reactor system The goal of this experimentation was to optimize formation of aromatics, specifically benzene, toluene, ethylbenzene, and xylenes (BTEX), for fuel blending or for use as feed stocks in the chemical industry. Large yields of both BTEX and light paraffin were observed when cracking canola oil over the protonated form of ZSM-5, a.k.a., HZSM-5, in comparison to the other zeolites the inventors have used to crack canola oil, for example, in comparison to zeolite-β. After conducting cracking experiments contacting canola oil with HZSM-5, the inventors conducted similar cracking experiments contacting canola oil with GaZSM-5, with a goal of further increases in BTEX yields. Excellent BTEX yields were obtained in the GaZSM-5 experiments, with said yields being significantly higher than those obtained with the protonated zeolite form. The inventors believe that the gallium-doped catalyst effectively convert light paraffins formed in the cracking process to aromatics, while also converting high-carbon-number components of the renewable oil to BTEX. The inventors believe the gallium-doped catalyst increases olefin production due to the dehydrogenation capability of the gallium, and that the catalyst dehydrogenates and cracks the C16 – C18 chains of the renewable oil to smaller olefins, especially C5+ olefins. Due to the shape selectivity of the catalyst, these C5+ olefins are then cyclized to C5 and C6 ring compounds which are further converted to aromatics. Thus, it is believed that the high BTEX selectivity of the catalyst when processing the renewable oils is due in some part to light paraffin conversion but also, importantly, to direct conversion of long chains to BTEX without first being cracked to C2 – C4. In this set of experiments, cracking canola oil over GaZSM-5 produced 39.3% BTEX, compared to cracking canola oil over HZSM-5, which produced 32.3% BTEX. Also, the GaZSM-5 reduced the ethane yield from 3.1% to 0.25% and the propane yield from 21.8% to 14.6%.

[0090] Experimental

[0091] Gallium-doped HZSM-5 was prepared at Ga/framework-Al ratios of 1/10, 1/3, and 1/1; meaning that roughly 1/10, 1/3, or all of the cation sites hosted Ga cations. In the case of 1/10 and 1/3 Ga/framework-Al ratios, the remaining cation sites still hosted protons. The first step in production of catalysts was to form pellets from powdered HZSM-5, which was Mobil ZSM-5 base catalyst purchased in powdered form from Zeolyst International. This was accomplished using Zeolyst CBV5524G powder (50/1 SiO_2/Al_2O_3) which was bound with 20 wt% Al_2O_3 and extruded into 1/16" pellets and calcined. The proton content of this material was measured using the temperature programmed desorption of n-propanamine and found to have an actual SiO_2/Al_2O_3 ratio of 61/1 (see V. Kanazirev, K.M. Dooley, G. Price, J. Catal. 146 (1994) 228–236 for this methodolgy) The 1/1 GaZSM-5 was then prepared by incipient wetness impregnation of a 25 g batch of HZSM-5 pellets with 4.77 g $Ga(NO_3)_3 \cdot xH_2O$, where x is determined by microbalance drying experiments to be approximately 9 - 11, dissolved in 22.97 g water. The wet catalyst was dried overnight in an oven at 120°C. The 1/3 and 1/10 catalysts were prepared in a similar fashion, using 1.52 and 0.51 g $Ga(NO_3)_3 \cdot xH_2O$, respectively. Prior to catalytic cracking, the Ga/HZSM-5 was heated to 500°C in flowing N_2 (converting the nitrate to the oxide), and then activated at 500°C under a 100 mL/min stream of 30% hydrogen in nitrogen. The activation process is known to accelerate the ion-exchange of Ga cations for protons in the zeolite.

[0092] Canola oil was cracked over a HZSM-5 material (that is, no gallium) at 350, 400, 450, and 500°C to determine which temperature would produce the most BTEX. The cracking results showed the most BTEX at 400°C, so the GaZSM-5 experiments were also done at that temperature.

[0093] The cracking experiments proceeded as follows:

a) 10 g of the zeolite catalyst was loaded into the reactor;
b) 10 g borosilicate glass beads were poured on top of the zeolite;
c) Reactor was loaded into the furnace;
d) N_2 flow was established;
e) For the Ga-containing materials, the reactor was brought to temperature for activation, and the catalyst was activated;
f) Reactor was brought to the cracking temperature;
g) Nitrogen co-feed was used during cracking, 0.0465 SLM (also used to dry the catalyst prior to reaction);
h) Canola oil feed was started, 0.182 mL/min (corresponding to WHSV = 1); and

i) Total amount of reactant fed, 10 g

[0094] The total mass balance for each run was performed based upon the difference between grams of reactant fed and product collected. Product collected was separated into three parts: 1) the gaseous product which is continuously measured by the micro-GC system, 2) a condensed liquid product which is collected from the reactor's effluent in a trap thermostatted at 0°C, and 3) the coke which is left on the catalyst. The mass of condensed liquid product was measured, then a water phase was separated from an organic phase, and the organic phase analyzed by simulated distillation and GC-MS. When spent catalyst charges were removed from the reactor, a small sample was used in a microbalance system to determine coke content. The rest of the spent catalyst was then subjected to coke removal in the calcining furnace using a synthetic air made of O_2 in Ar. The total vapor product recovered was determined by integrating the micro-GC measurements of the gaseous product composition over time and using the known N_2 flowrate as an internal standard.

[0095] Yields were calculated in weight-percent (wt-%), defined as Y = 100 x PF/RC, wherein Y equaled yield in weight %, PF equaled weight of product formed, and RC equaled weight of reactant converted. As the operating conditions selected for the experiments in all Examples gave 100 conversion of the oil reactant, RC is in the above equation is identical to what was fed to the reactor system.

[0096] On average, the mass balances in Table 7, below, accounted for 98% of the reactant. As shown in Figure 2, which portrays results from the preliminary runs SAP275-279 on HZSM-5 catalyst (no Ga), the yield of liquid products (triangles) generally decreased with increasing temperature, while the gas products (vapor products, squares) demonstrated the opposite trend, that is, generally increasing with increasing temperature. The yield of solid products did not vary appreciably with temperature.

[0097] Table 7. Reaction Conditions and Mass Balances for Example I (reactant in each experiment being 10 grams)

Experiment Number	Ga/ Framework-Al	Temp (C)	Vapor Products (g)	Liquid Products (g)	Solid Products (g)	Total Products (g)	Products-Feed Difference (%)
SAP276	0	350	3.93	5.32	0.45	9.70	-2.97
SAP278	0	400	3.92	5.54	0.37	9.83	-1.68
SAP279	0	450	3.79	5.26	0.38	9.43	-5.71
SAP275	0	500	4.29	5.05	0.42	9.76	-2.36
SAP281	1.0	400	3.31	5.86	0.48	9.65	-3.51
SAP282	0.33	400	3.83	5.45	0.48	9.76	-2.42
SAP283	0.1	400	4.11	5.36	0.40	9.87	-1.31
SAP284	0	400	4.13	5.21	0.37	9.71	-2.87
SAP286	0	400	4.12	5.26	0.39	9.77	-2.29
SAP287	0	400	4.27	5.22	0.36	9.85	-1.53

[0098] Adding gallium to the HZSM-5 (runs SAP281-283) had a much more pronounced effect, seen in Figure 3, about twice as much as the change in temperature. The gallium increased the liquid yield, while decreasing the yield of gas, compared to the average of runs SAP284-287. Vapor product yields changed with increasing amounts of gallium added to the catalyst for experiments SAP281-283, particularly for propane and ethane. The molecules shown in Figure 3 represent ~98% of all vapor products from each experiment. Results for 0.0 Ga are the mean of SAP284-287 and the “error bars” show the 95% confidence interval.

[0099] As shown in Figure 4, increasing Ga content (SAP281-283) increased the yield of liquid (triangles), while coke (circles) stayed almost constant and the amount of vapor products (squares) decreased compared to the mean of SAP284-287 (no Ga).

[0100] Product Analysis

[0101] In the gas phase product (see Figure 3), the propane yield decreased from 21.8% to 14.6% as the Ga content went up. Likewise, the ethane yield went from 3.1% to 0.25%, while the hydrogen yield increased from 0.3% to 1.2%.

[0102] Though the experiments were not performed in an effort to make gasoline, but to make aromatics, the inventors still characterized the liquid product by simulated distillation. This is shown in Figure 5, which portrays boiling point distribution of the organic phase products. The majority of the products fall in the 60-188°C range, which is typical for ZSM-5 catalysts that primarily produce BTEX.

[0103] The gasoline range material is the fraction which boils below 225°C. Gasoline requirements (D4814) specify that 10, 50, 90, and 100% of the fuel should boil by certain temperatures, respectively called T10, T50, T90, and FBP (final boiling point). The FBP is fixed at 225°C, but the other temperatures vary both seasonally and regionally. These temperatures provided the break points for evaluating the composition of the organic phase liquid products shown in Figure 5. HZSM-5 is well known for producing high yields of BTEX, which all have boiling points in the 60-188°C range. However, the gallium-doped catalyst performed significantly better than the HZSM-5 in BTEX production, as evidenced by the yields shown in Figure 5. As Ga/framework-Al increased from 0 to 1.0, the yield of products between 60 - 188°C increased from 34.6% to 40.8% based on canola oil converted.

[0104] As shown in Figure 6, the liquid products were also analyzed by GC-MS to quantify the BTEX content, which increased with the gallium content of the ZSM-5 catalyst. The benzene (B.P. 80.1°C) yield increased from 7.5% to 8.4% as the Ga/framework-Al increased from 0 to 1.0 and comprised nearly all the material in the 60-93.5°C range. Toluene (B.P. 110.6°C) behaved similarly and had the greatest change in yield, going from 15.4% up to 19.3%. It also made up just over half of the material in the 93.5-188°C boiling point range. The C8 aromatic yields (ethylbenzene, B.P. 136°C; p-xylene, B.P. 138°C; m-xylene, B.P. 139°C; o-xylene, B.P. 144°C) also increased, from 9.5% to 11.6%, with the increasing gallium content in the catalyst. [0064] For the 1.0 Ga/framework-Al material, the total BTEX yield increased by 7.0 percentage points, so that BTEX comprised 77.3% of the organic liquid product. Aromatics heavier than the C8 fraction are present in the organic liquid phase, but these are more difficult to quantify and are generally less valuable than the BTEX fraction.

[0105] Example I Conclusions

[0106] HZSM-5 catalysts are well known for their ability to produce high levels of benzene, toluene, and xylenes. Cracking canola oil with a standard HZSM-5 catalyst yielded about 32.3% BTEX at 400ºC, but, by adding gallium to the catalyst, the inventors observed an increase in the BTEX yield, of 7 wt-%, to achieve about 39.3% under the same conditions. These BTEX aromatics comprised 77% of the organic liquid products, so, in addition to representing a possible renewable source of aromatics for the chemical industry, it might be possible to blend it directly into kerosene or diesel to obtain a jet fuel nearly identical to Jet A-1. Additional testing will be needed to measure the products from these experiments for the chief properties of jet fuel, such as freezing point, vapor pressure, viscosity, flash point, and heat of combustion.

Example II: Catalytic Conversion of Canola Oil to Aromatics by Two Reactors in Series

[0107] Catalytic conversion of canola oil to aromatics was conducted using two reactors in series. The goal of the work in this Example was to optimize the formation of benzene, toluene, ethylbenzene, and xylenes (BTEX), which are valuable for gasoline or use as chemicals. Canola oil cracking on H-ZSM-5 has been shown to generate substantial amounts of light paraffins, for example, 25 wt% oil fed, as shown in Example I. This Example continues experimentation directed toward achieving “green BTEX” production, by increased conversion of light paraffins to BTEX and, the inventors believe, by direct conversion of long chains to BTEX. In this Example, a multiple-reactor system is employed wherein vapor products from a primary reactor cracking canola oil over H-ZSM-5 or GaZSM-5 were fed to a secondary reactor containing GaZSM-5 and converted to BTEX. In this reactor system, “primary” means the first reactor to which the oil feedstock is fed, and "secondary" means the second reactor to which the gas/vapour effluent from the primary reactor is fed.

[0108] The secondary reactor containing GaZSM-5 raised the BTEX yield achieved from cracking canola oil over H-ZSM-5 (in first reactor) from 39.5 wt% oil fed to 43.8 wt%, that is, an increase of 4.3 wt-% yield. The secondary reactor containing GaZSM-5 also raised the BTEX yield achieved from cracking canola oil over GaZSM-5 (in the first reactor) from 46.3 wt% oil fed to 51.2 wt%, that is, an increase of 4.9 wt-% yield. Note also that the BTEX yields achieved when both reactors contained gallium-doped catalyst (46.3 wt-% and 51.2 wt-%) were both significantly higher than the BTEX yields achieved when protonated catalyst was followed by the gallium catalyst (39.5 wt-% and 43.8 wt-%).

[0109] Catalysts

[0110] The cracking experiments using the protonated form of ZSM-5 catalyst used Zeolyst H-ZSM-5 with a 25/1 Si/framework-Al ratio.. The experiments using the Ga cracking catalyst also used the same Zeolyst H-ZSM-5 material, with gallium loaded by incipient wetness addition of $Ga(NO_3)_3$ at a loading of 1 Ga/framework-Al. The terminology "GaZSM-5(1-1)" is used to emphasize that the loading is 1 Ga – 1 Al.

[0111] Experimental

[0112] The cracking process was performed in a two- reactor configuration, made up of two reactors in series shown in Figure 1B. Both reactors were mounted vertically within the furnace. A thermocouple was centered in each reactor tube to monitor the temperature in the catalyst bed. This temperature was taken as reaction temperature and was maintained at a constant set-point by a LabVIEW based control program that adjusted the furnace power. The liquid product from the first reactor (11 mm I.D. and 521 mm overall length) was condensed in the glass cylinder and the vapor product entered the second reactor (11 mm I.D. and 419 mm overall length) for further reaction. The liquid product from the second reactor was condensed in the glass cylinder and the vapor product flowed to a Micro GC (Agilent G2804A) that analyzed the gas composition every four minutes.

[0113] The details of the two- reactor system 10' of Figure 1B are called-out as follows: nitrogen cylinder 51, gas regulator 52, valve 53, mass controller 54, syringe pump 55, first (primary) reactor 56, catalyst 57 in primary reactor, first (primary) furnace 58, thermocouple in the primary reactor (not shown), glass cylinder 60, ice-cooled condenser 61, liquid products 62, secondary furnace 63, secondary reactor 64, catalyst 65 in secondary reactor, glass cylinder 66 and ice-cooled condenser 67 for secondary reactor effluent, liquid products 68 of secondary reactor effluent, and gas chromatograph 67.

[0114] Two experiments were conducted at atmospheric pressure. The first experiment was done with H-ZSM-5 loaded in the first reactor, and GaZSM-5(1-1) in the second reactor. A second experiment was done with GaZSM-5(1-1) loaded in both reactors in series. Reaction temperatures were set according to the performance of the loaded catalysts, wherein the optimum reaction temperatures, determined in previous experimentation, of H-ZSM-5 and GaZSM-5(1-1) for cracking canola oil are 400°C and 350°C, respectively. So, the first reactor (receiving canola oil as feed) was set at reaction temperature 400°C when containing H-ZSM-5, and 350°C when containing GaZSM-5. The second reactor, containing GaZSM-5(1-1) for both experiments, was set to 450°C to convert the vapor products from the first reactor, based on the inventors' earlier work that showed 450°C was the optimum temperature for propane conversion to BTEX over GaZSM-5(1-1). In both cases, the first reactor contained 10 g catalyst and the second reactor contained 5 g catalyst. Experiment SAP359 is the experiment number for the run wherein H-ZSM-5 was followed by GaZSM-5(1-1) (primary and secondary reactors, respectively), and experiment SAP360 is the experiment number for the run wherein GaZSM-5 was followed by GaZSM-5 (primary and secondary reactors, respectively).

[0115] Before catalytic conversion, GaZSM-5(1-1) was heated to 500°C in flowing nitrogen and then activated at 500°C under a 100 ml/min stream of 30% hydrogen in nitrogen for at least 1 hr. The activation process drives Ga cations into the zeolite pores and it replaces protons in the zeolite. After the activation step, the reactor was cooled to the desired reaction temperature. Co-feed nitrogen was set to 46.5 ml/min and the canola oil flow rate was set to 0.182 ml/min. The experiment lasted about 2 hrs and 20 g reactant was fed over that time period.

[0116] The total mass balance for each run was performed based upon the difference in grams of the reactant fed and products collected. The products mainly comprise three parts, gas, liquid and coke. Table 8 gives the reaction conditions and product mass obtained from canola oil cracking in each reactor, as well as the total mass balances. The mass balance was within 5 wt%

for these two runs. Table 9 contains the composition of the products summarized in Table 8 calculated as the weight percent of total oil fed.

[0117] Table 8. Overall mass balances for conversion of canola oil in two reactors in series, for Example II

SAP359

	Catalyst	Temp (ºC)	Gas (g)	Liquid (g)	OLP (g)	Aqueous (g)	Residue (g)	Coke (g)
Reactor 1	HZSM-5	400	-	9.35	9.35	0	0.47	0.26
Reactor 2	GaZSM-5	450	10.03	0.29	0.29	0	0.05	0.05

SAP360

	Catalyst	Temp (ºC)	Gas (g)	Liquid (g)	OLP (g)	Aqueous (g)	Residue (g)	Coke (g)
Reactor 1	GaZSM-5	350	-	11.48	10.69	0.79	0.49	0.56
Reactor 2	GaZSM-5	450	7.21	0.5	0.5	0	0.11	0

Totals

	Oil Fed (g)	Gas (g)	Liquid (g)	OLP (g)	Residue (g)	Coke (g)	All Products (g)	Difference
SAP359	20.00	10.03	9.64	9.64	0.52	0.31	20.50	2.50%
SAP360	20.00	7.21	11.98	11.19	0.60	0.56	20.35	1.75%

[0118] Table 9. Yield of product or groups obtained from conversion of canola oil in two reactors in series, for Example II

	SAP359 (1st reactor protonated catalyst, 2nd reactor gallium catalyst)		SAP360 (both reactors gallium catalyst)	
Yield of components or groups in the gas product				
Methane	10.13%		6.53%	
Ethane	9.06%		3.82%	
Propane	7.08%		6.36%	
Butanes	0.23%		0.18%	
Pentanes	0.00%		0.01%	
Hexanes+	9.81%		8.13%	
Hydrogen	1.27%		2.03%	
Olefins	0.43%		0.31%	
CO+CO2	12.12%		8.71%	
Yield of components or groups in the organic liquid product (OLP)				
	Reactor 1	Reactor 2	Reactor 1	Reactor 2
0-60ºC	0.26%	0.00%	0.44%	0.00%
0-93.5ºC	9.96%	0.30%	9.58%	0.58%
0-188.1ºC	36.78%	1.14%	42.98%	2.08%
0-225ºC	39.74%	1.26%	45.65%	2.26%
225ºC above	7.01%	0.19%	7.80%	0.24%
Yields of aromatics in the OLP				
Benzene	10.07%	0.31%	9.76%	0.59%
Toluene	16.18%	0.55%	20.65%	1.01%
Xylenes	6.70%	0.21%	10.71%	0.37%
Total BTEX	43.82%		51.22%	
Total Gasoline range	50.81%		56.04%	

[0119] The 9.81 wt% hexanes+ yield of the SAP359 gas product was particularly high, compared to the 2.4 wt% yield of hexanes+ in SAP284-287 (cracking canola oil over H-ZSM-5 at 400°C, see Example I). This led the inventors to suspect that the BTEX products were not completely condensing upon leaving the second reactor. Therefore, three gas product samples were taken during SAP360 at 30 minute intervals and analyzed using an Agilent 5975 GC-MS to identify the vapor phase products, especially the hexane+ fraction reported by the micro-GC. The GC-MS was set up to only identify molecules larger than C3. The flame ionization detector showed 4 primary peaks, which were identified by the mass spectrometer as benzene, toluene, and xylenes. Some other molecules were present, but in such low concentrations that they could not be identified. So, the hexanes+ in the gas as analyzed by the micro-GC can be regarded as principally aromatics and were included in the BTEX and gasoline range yield totals.

[0120] Feeding the vapor products from the primary reactor to a second reactor loaded with GaZSM-5 increased the overall organic liquid product (OLP) yield in the canola oil cracking as expected. See, in Table 8, that the OLP yield from the first reactor in the SAP359 run was 9.35 g, and that the second reactor of that run added 0.29 g of OLP. See also, that loading gallium-doped catalyst in both reactors, in run SAP360 increased OLP further, as may be seen by comparing 11.19 g OLP in SAP360 to 9.64 g OLP in SAP360.

[0121] Example II Conclusions

[0122] Adding another reactor to convert vapor product obtained from canola oil cracking can improve OLP yield and BTEX yield. The hexanes+ fraction in the gas products are un-condensed aromatics. The best total yields of BTEX in this Example were achieved when all (both) reactors were loaded with gallium-loaded catalyst. Specifically, cracking canola oil over GaZSM-5 at 350°C produced 46.3% BTEX (assuming hexanes+ were un-condensed aromatics), and adding the second reactor loaded with GaZSM-5 at 450°C increased the total BTEX yield to 51.22 wt%. As noted above in this Example, the BTEX yield of 39.45 wt% from cracking canola oil over H-ZSM-5 at 400°C increased to 43.82 wt% with the addition of the second reactor containing GaZSM-5 catalyst at 450°C. The inventors recognize that further improvements in aromatics yield may be made with further experimentation. Possible optimization parameters include gallium loading levels in both reactor beds, amount of catalyst in each bed, temperatures of each bed, space velocities relative to feedstocks flowrate and relative to nitrogen feed, and other possible parameters.

Example III Comparison of Algae Oil Cracking over GaZSM-5 and HZSM-5

[0123] Algae oil (sample NL-72-32-03) was subjected to catalytic cracking over a gallium-doped ZSM-5 (GaZSM-5, 1.0 Ga/framework-Al in the zeolite) and the proton form of ZSM-5 (HZSM-5) at 400°C. The goal of this work was to compare the formation of aromatics from algae oil between these two catalysts, specifically benzene, toluene, ethylbenzenes, and xylenes (BTEX), for fuel blending or for use as feedstocks in the chemical industry. It was observed that GaZSM-5 produced more BTEX and less paraffins (especially propane) compared to HZSM-5, during algae oil cracking at the same reaction temperature.

[0124] The experiments were performed with the 20 g scale reactor system, with a single reactor, as described above for Example I, loaded with 10 g of catalyst. The results of these experiments showed that cracking algae oil (NL-72-32-03) over GaZSM-5 gave 46.8 wt% yield of BTEX and 48.3 wt% yield of gasoline, compared to 38.9 wt% yield of BTEX and 42.9 wt% yield of gasoline when cracking algae oil over HZSM-5 under the same conditions. Also, GaZSM-5 reduced the C_1-C_3 paraffin yield, producing 16.7 wt% C1-C3 paraffin, compared to 25.9 wt% for HZSM-5. GaZSM-5 also reduced propane yield, producing 6.4 wt% propane, compared to 14.0 wt % for HZSM-5.

[0125] Experimental

[0126] GaZSM-5 was made according to the methods reported in Example I starting with the same Zeolyst CBV5524G powder (50/1 SiO2/Al2O3) which was converted into pellets as in Example I then loaded with gallium in an identical way to Example I. However, the only gallium loading level which was used in this study corresponded to 1.0 Ga/framework-Al in the zeolite, referred to in this Example as “GaZSM-5.” The base ZSM-5 material was used in its fully protonated form referred to as “HZSM-5.” Since HZSM-5 gave the highest BTEX yield at 400°C for a canola oil feedstock in previous work, the algae oil cracking experiments were also done at that temperature. The GaZSM-5 catalyst was activated at 500°C under a 100 ml/min stream of 30% hydrogen in nitrogen for at least 1 hour. This activation process is known to accelerate the ion-exchange of Ga cations for protons in the zeolite. For HZSM-5, as usual, the catalyst was dried at 400°C with nitrogen flow rate of 46.5 ml/min for 2 hours prior to utilization as a cracking catalyst. Assuming a density of 0.9 g/ml for the algae oil, 10 g of algae oil corresponds to 11.1 ml and the algae oil flow rate was 0.185 ml/min, which corresponds to WHSV=1.0. Cracking experiments proceeded as follows:

- 10 g of the zeolite catalyst was loaded into the reactor
- Reactor was loaded into the furnace
- N_2 flow was established
- For GaZSM-5, the reactor was brought to 500°C, and the catalyst was activated
- Reactor temperature was set to 400°C
- Nitrogen co-feed was established at 0.0465 SLM
- Algae oil feed was started, 0.185 ml/min (corresponding to WHSV = 1.0)
- Total amount of reactant fed, 11.1 ml or 10 g

[0127] As usual, the total mass balance for each run was performed based upon the difference between grams of reactant fed and product collected. Product collected was separated into three parts: 1) the gaseous product which was continuously measured by the micro-GC system, 2) a condensed liquid product which was collected from the reactor's effluent in a trap thermostatted at 0°C, and 3) the coke which was left on the catalyst.

[0128] Table 10 gives the overall mass balances obtained from algae oil cracking over GaZSM-5 and HZSM-5. It can be seen clearly GaZSM-5 produced more liquid and less gas compared to HZSM-5. The detailed product analysis is discussed below.

[0129] Product Analysis

[0130] Table 10. Reaction Conditions and Mass Balances for Algae Oil in Example III (reactant in each experiment being 10 grams)

Experiment Number	Catalyst	Temp (°C)	Vapor Products (g)	Liquid Products (g)	Solid Products (g)	Total Products (g)	Products-Feed Difference (%)
SAP383	GaZSM-5	400	3.84	5.59	0.77	10.20	2.0
SAP384	HZSM-5	400	4.62	4.97	0.67	10.26	2.6

[0131] In the gas phase product (see Figure 7), the C1-C3 paraffin yield decreased with the addition of gallium to the catalyst. For example, the propane yield decreased from 14.0 wt% to 6.4 wt%. GaZSM-5 gave a 2.0 wt % yield of hydrogen, compared to HZSM-5 giving only 0.5 wt% yield of hydrogen.

[0132] The liquid products were also analyzed by GC-MS to quantify the BTEX content. Gasoline yield was obtained via simulated distillation. GaZSM-5 produced almost 40.8 wt% yield of BTEX in the liquid product, compared to HZSM-5 producing 34.1 wt% yield of BTEX. By the simulated distillation, GaZSM-5 gave 42.4 wt% yield of gasoline in the liquid and HZSM-5 gave 38.1 wt%. By adding gallium to the HZSM-5 catalyst, BTEX yield and gasoline yield were increased by 6.7 wt% and 4.3 wt%, respectively, in the liquid phase. It also showed that BTEX are the major products in the gasoline for these two materials. For the GaZSM-5, the composition of BTEX in the gasoline is as high as 96.4 %, compared to 89.6% for the HZSM-5.

[0133] In previous experiments, the actual components corresponding to hexanes+ were identified, which are reported by the gas analysis instrument (the micro-GC), and that species turns out to be almost pure benzene. This makes sense since the C_6 fraction in the collected liquid product is almost exclusively benzene (as determined by GC-MS), and since the off-gas is nearly in vapor-liquid equilibrium with the collected liquid. Therefore, if the hexanes+ yield from the vapor phase is determined and added into the benzene yield in the liquid phase, the overall yields from the two catalysts may be calculated.

[0134] Figure 8 shows the overall yields obtained from these two catalysts. For the GaZSM-5 material, the overall BTEX yield and gasoline range product yield were 46.8 % and 48.3%, respectively, with 96.9% of gasoline range molecules being BTEX. The composition of BTEX in the liquid product (including hexanes+) was 83.6%. These excellent yields may be compared to those for HZSM-5, which were 38.9 % overall BTEX yield and 42.9 % gasoline yield. For HZSM-5, 90.7% of the gasoline fraction was BTEX, and 78.2% of the total liquid product (including hexanes+) was BTEX. Therefore, Figure 8 shows that the total BTEX yield ("overall BTEX yield") was increased by 7.9% by adding gallium to the HZSM-5, and gasoline yield was also increased by 5.4%.

[0135] Conclusions from Example III, and Comparison of Example I (Canola Oil) and Example III (Algae Oil)

[0136] Adding gallium to HZSM-5 increases BTEX yield and gasoline yield for algae oil cracking at 400°C. GaZSM-5 also produced significantly more hydrogen than HZSM-5, which is consistent with an increased aromatics production.

[0137] One may compare the results from cracking canola oil vs. algae oil, on the preferred catalyst (GaZSM-5, 1.0 Ga/framework-Al in the zeolite), by reviewing Example I (Run SAP281) and Example III (SAP383). These two runs used a single reactor and substantially the same conditions operating conditions and catalyst, but Example I, SAP281, processed only canola oil and Example III, SAP 383, processed only algae oil. Note that both SAP281 and SAP383 were both conducted at 400 degrees C reactor temperature. Cracking of canola oil with the preferred gallium-doped catalyst produced a BTEX yield of 39.3 wt-% and a gasoline range (60 – 225 degrees C) yield of approximately 43 wt-%. On the other hand, cracking of algae oil with the preferred gallium-doped catalyst produced a BTEX yield of 46.8 wt-% and a gasoline range (60 – 225 degreed C) of 48.3 wt-%. Thus, under the same or substantially the same process, it is remarkable that algae oil produced 7.5 wt% more BTEX and approximately 5 wt-% more gasoline, compared to canola oil.

Example IV: Catalytic Conversion of Fossil Petroleum Gas Oil over Ga/ZSM-5 and HZSM-5

[0138] This Example describes the catalytic cracking of gas oil (from Conoco Phillips) over HZSM-5 and Ga-doped ZSM-5 (GaZSM-5) at 400 degrees C, for comparison to canola oil and algae oil results from Examples I and III. The goal of this work was to compare the formation of aromatics between these two catalysts, specifically benzene, toluene, and xylenes (BTEX), for fuel blending, or for use as feedstocks in the chemical industry. It was observed that Ga/ZSM-5 produced more BTEX and less paraffins (especially propane) compared to HZSM-5 gas oil cracking at the same reaction temperature. However, the boost in BTEX yield when Ga was added to the catalyst was much greater for the renewable oils (algae and canola oils) and the overall gasoline yields are also greater for the renewable oils.

[0139] Experimental

[0140] GaZSM-5 was made according to the method reported in Example I, but the only gallium loading level that was used in this Example corresponded to 1.0 Ga/framework-Al in the zeolite (Ga/ZSM-5). The base ZSM-5 material was used in its fully protonated form (H-ZSM-5). Because H-ZSM-5 gave the highest BTEX yield at 400 degrees C for algae oil feedstock in Example III, the gas oil cracking experiments of this Example were also done at this temperature. The Ga/ZSM-5 catalyst was activated at 500 degrees C under a 100 ml/min stream of 30% hydrogen in nitrogen for at least 1 hour. This activation process is known to accelerate the ion-exchange of Ga cations for protons in the zeolite. For H-ZSM-5, as usual, the catalyst was dried at 400oC with nitrogen flow rate of 46.5 ml/min for 2 hours prior to utilization as a cracking catalyst. The density of the gas oil was calculated to be 0.88 g/ml, so that 10 g of gas oil corresponded to 11.4 ml and the gas oil flow rate was 0.189 ml/min to correspond to WHSV=1.0.

[0141] The gas oil cracking experiments may be summarized as follows:

a) 10 g of the zeolite catalyst was loaded into the reactor;
b) Reactor was loaded into the furnace;
c) N2 flow was established (46.5 ml/min);
d) For Ga/ZSM-5, the reactor was brought to 500°C, and the catalyst was activated;
e) 30% Hydrogen flow in nitrogen for 1 hr;
f) Reactor temperature was then decreased to reaction conditions;
g) Reactor temperature was set to 400°C;
h) Gas oil feed was started, 0.189 ml/min (corresponding to WHSV = 1.0); and
i) Total amount of reactant fed, 11.4 ml.

[0142] The total mass balance for each run was performed based upon the difference between grams of reactant fed and product collected. Product collected is separated into three parts: 1) the gaseous product which, is continuously measured by the micro-GC system, 2) a condensed liquid product which, was collected from the reactor's effluent in a trap and glass adapter at 0°C, and 3) the coke which, is left on the catalyst and simply measured by mass difference between the fresh and used catalyst. Table 11 gives the overall mass balances obtained from gas oil cracking over Ga/ZSM-5 and H-ZSM-5. It can be seen clearly Ga/ZSM-

5 produced more liquid and less gas compared to H-ZSM-5. The detailed product analysis is discussed below.

[0143] Table 11. Mass Balance and Reaction Conditions for Gas Oil Cracking Experiments

Experiment	Catalyst	Temp (°C)	Reactant (g)	Vapor Product (g)	Liquid Product (g)	Solid Product (g)	Total Product (g)	Difference
SB_SAP 001	HZSM-5	400	10.00	2.91	6.71	0.77	10.39	3.9%
SB_SAP 002	GaZSM-5 (1:1)	400	10.00	1.95	7.31	0.77	10.02	0.2%

[0144] Products Analysis

[0145] Figure 9 shows the gas phase products produced during cracking of gas oil. It is clear that the C1-C3 paraffin yield decreased with doping of the zeolite with gallium, and the amount of propane decreased by a factor of three. It is also clear that a higher amount of hydrogen product was present in the run utilizing Ga/ZSM-5 compared to the run utilizing H-ZSM-5. The increased hydrogen product with the gallium-doped zeolite correlated well with the previous work involving algae (Example III) and canola oil (Example I) cracking over Ga/ZSM-5, showing that an increased amount of BTEX is formed through the addition of Ga.

[0146] In the previous Examples, the actual components corresponding to Hexanes+ were identified by micro-GC to be almost pure benzene. This was considered reasonable, because the C6 fraction in the collected liquid product was almost exclusively benzene, as determined by GC-MS, and because the off gas is nearly in vapor-liquid equilibrium with the collected liquid. Therefore, for this Example, if we take the Hexanes+ yield from the vapor phase, and add it into the benzene yield in the liquid phase, the overall yields from the two catalysts can be calculated.

[0147] The liquid products were also analyzed by GC-MS to quantify the BTEX content, and these results are included in Table 12, below. For comparison purposes, results from cracking of canola oil (Example I) and cracking of algae oil (Example III) are also included in Table 12. For comparison purposes, the results from cracking of gas oil (this Example) are plotted beside the results from cracking of algae oil (Example III) in Figure 10. Regarding the gas oil feedstock, Ga/ZSM-5 produced 40.64% yield of BTEX in the liquid product, compared to a 39.24 wt% yield by the H-ZSM-5. Adding Ga to H-ZSM-5 caused the BTEX yield from gas oil to increase by only 1.6 wt%, compared to about a 7% improvement in BTEX yield when Ga was added to the catalyst for the canola and algae oil feedstocks. The data also showed that BTEX were the major products in the gasoline for this feed stock.

[0148] Table 12. Yields of benzene, toluene, ethylbenzene, xylenes, total BTEX, and Gasoline in wt% for various feed stocks and catalysts. All experiments run at 400°C and WHSV = 1.0.

	Canola Oil		Algae Oil		Gas Oil	
Catalyst	1.0 Ga-ZSM-5	H-ZSM-5	1.0 Ga-ZSM-5	H-ZSM-5	1.0 Ga-ZSM-5	H-ZSM-5
Benzene	8.38	7.45	10.74	7.65	13.96	10.44
Toluene	19.31	15.40	19.03	15.46	18.59	18.35
m-, p-Xylene	8.10	6.32	7.14	6.95	5.24	6.69
o-Xylene	2.28	1.78	2.08	2.04	1.56	1.99
Ethylbenzene	1.20	1.35	1.83	2.02	1.30	1.82
BTEX	39.27	32.29	40.82	34.12	40.64	39.29
Gasoline	43.63	37.67	48.86	42.86	48.65	48.56

[0149] A simulated distillation of the Conoco Phillips gas oil is compared to the simulated distillation of algae oil in Figure 11. Simulated distillation of the canola oil is not shown in Figure 11 because canola oil breaks down before it vaporizes. These feedstock simulated distillation curves may be compared to the product simulated distillations that are given in Figure 12. Gasoline yields of each of the products from gas oil, canola oil, and algae oil over the H-ZSM-5 and GaZSM-5 catalysts were also obtained via simulated distillation, and these results are included in the last line of Table 12. It may be noted that, when the feedstock was gas oil, addition of Ga had virtually no effect on the gasoline yields, which were about 48% in both cases. However, for the renewable oils, a significant effect of the addition of Ga was noted.

[0150] Figure 12 also shows how much different the products from the various feedstocks were. The renewable oils produced much lighter liquid products than the gas oil produced. Furthermore, since the algae oil and canola oil feedstocks were heavier than gas oil, a much greater disparity in the overall reduction in boiling point distribution of the feedstock resulted when the renewable oils were the feedstocks.

[0151] Conclusions from Example IV

[0152] It may be concluded that, in the gas oil cracking processes of this Example, the addition of Ga did increase the overall BTEX yield slightly but it had little to no effect on the overall gasoline yield. This was in contrast to the same experiments using canola (Example I) and algae oil (Example III), where large yield increases in BTEX and gasoiline were seen when Ga was added to the catalyst. Also, liquid products from the renewable oils were much lighter than the liquid products from gas oil, leading to a conclusion that, overall, the renewable oils were easier to crack. Thus, it may be said that the gallium-modification produced a surprising result in terms of increased BTEX yields and gasoline yields from renewable oils, including algae oil, while the gallium-modification had little or no effect on BTEX and gasoline yields from gas oil. The little or no effect on gas oil may suggest that providing a gallium-cation catalyst additive to an FCC unit may be effective in increasing aromatics production from the algae oil or other renewable oil while not harming BTEX and gasoline yields from the gas oil to any significant extent.

Example V: FCC Cracking of Algae Oil

[0153] In a loaded-in-part (gallium-cation catalyst) and fed-in-part (algae oil) FCC operation, the majority of the FCC catalyst would be maintained as conventional FCC cracking catalyst (such as Y zeolite) and the majority of the feedstock would be maintained as a conventional FCC feed (such as gas oil/vacuum gas oil). Therefore, the yield structure and coke-on-catalyst obtained from algae oil, under conventional FCC conditions and with conventional FCC catalyst, are of great interest. This Example illustrates certain embodiments of fluid catalytic cracking of algae oil compared to fluid catalytic cracking of vacuum gas oil. For additional information regarding the structure and function of a conventional FCC unit, refer to Example VIII and Figure 23.

[0154] An algae oil was obtained from *Nannochloropsis salina* by HTT hydrothermal-treatment and heptane solvent extraction, according to method steps a – j listed above in the section entitled “Alternative Techniques of Obtaining Crude Algae Oil from Biomass”. The hydrothermal treatment step (step b in the method listed above) was conducted at 260 C for 0.5 hour. See the “Algae Oil Feed” analysis in Tables 4 – 6, above.

[0155] The algae oil feed was catalytically cracked in a Micro Catalytic Cracking (MAT) system. MAT equipment and tests are well known in petroleum refining R & D, and have been designed and evolved over the years to be highly correlated with large-scale fluidized catalytic cracking (FCC) units. The predictive ability of MAT tests is rather remarkable considering they require only grams of feed, whereas commercial FCC units can process over 100 mbpd of feed. The MAT tests, like commercial FCC units, operate at cracking temperatures of about 1000 degrees F and with very short catalyst-feed contact times (1 – 5 seconds), and use zeolite-based catalysts at atmospheric pressure.

[0156] In this Example, MAT testing was used to compare FCC processing of algae oil feed (“crude algae oil”) and FCC processing of a reference petroleum feedstock from a European refinery, specifically, a petroleum-derived vacuum gas oil (VGO) containing roughly 10 mass % resid, having an API of 22, and a sulfur level of 0.61 wt%. Table 13, below, shows the yield structure in MAT testing of the standard VGO (first column of data) and the algae oil feed (second column of data), with the difference calculated and shown in the third data column.

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[0157] Table 13. FCC MAT Testing of Extracted Algae Oil Feed compared to Standard VGO Feed

	Yields (wt%)		
	Standard VGO Feed	Extracted Algae Oil Feed	Difference Algae Oil – VGO
C/O ratio	1.981	2.008	0.026
Conversion	50.514	49.885	-0.629
Gasoline(C5-421° F)	40.623	29.286	-11.337
Coke yield	2.296	10.047	7.751
LCO yield	18.236	35.631	17.395
LPG yield	6.001	5.536	-0.465
H2+C1+C2+H2S	1.512	3.225	1.713
H2+C1+C2	1.512	3.225	1.713
T.C3	3.228	2.313	-0.916
T.C4	2.772	3.223	0.450
C4=/ Tot. C4's	0.705	0.759	0.055
C3=/ Tot. C3's	0.867	0.528	-0.340
H2	0.148	0.063	-0.085
H2S	0.000	0.000	0.000
CH4	0.544	1.030	0.486
C2+	0.412	1.193	0.782
C2=	0.408	0.938	0.530
C3+	0.428	1.092	0.664
C3=	2.800	1.221	-1.580
iC4+	0.674	0.269	-0.405
nC4+	0.145	0.506	0.361
iC4=	0.803	1.111	0.308
nC4=	1.150	1.337	0.187
C4=	1.953	2.447	0.494
C4= =	0.082	0.000	-0.082
DCO	31.250	14.484	-16.766
wt% recovery	96.276	98.929	

[0158] Figure 13 compares the conversion (percent of the feed converted to distillate and to lighter components such as gasoline, plus coke) at a range of catalyst-to-oil ratios (C/O) for the algae oil feed and the reference petroleum VGO feed. In this test, the algae oil has approximately the same reactivity as the reference VGO; this may be inferred by noting that the algae oil feed has a comparable conversion of about 50% to the VGO at the same C/O ratio.

[0159] Figure 14 shows that the coke yield for the algae oil feed is significantly higher than for the VGO. This is important because commercial-scale FCC units operate in such a way that the heat balance drives the conversion of feeds to lower levels when they have high coke yields. Consequently, the algae oil feed of this Example is expected to exhibit much lower conversion than VGO in commercial units due to its high coke yield.

[0160] The yields of gasoline, LCO (distillate range material), DCO, TC2, TC3, and TC4 from the algae oil and VGO are shown in Figures 17 – 22, respectively. Note that the corresponding yields from hydrotreated algae oils, in Example VII below, are also shown in Figures 17 – 22, for study of the effect of hydrotreating prior to FCC processing.

[0161] In an FCC unit, higher coke yields are favored by heavier compounds (especially 1000 degrees F + material) and basic nitrogen-containing compounds in the feed to the unit. The later react with and poison the acidic catalytic sites in the zeolite used as the cracking catalyst, thus making coke and also reducing conversion. Oxygen-containing compounds may also contribute to increased coke yields, and, separately, to lower conversions.

[0162] Therefore, in a catalytic cracking process, the algae oil feed of this Example exhibits coke yields that may be problematic for many FCC units. This suggests that inclusion of this unhydrotreated algae oil feed in an existing FCC unit as a significant percent of the total feed would lower the overall conversion in the FCC unit (compared to the "base-line" operation without the algae oil feed) due to the impact of the coke on the unit heat balance. Therefore, certain unhydrotreated algae oils (for example, certain unhydrotreated HTT hydrothermally-treated and solvent-extracted algae oils), may be a concern regarding coke on conventional FCC catalysts. This may impact certain embodiments of gallium-cation catalyst loaded-in-part, and algae oil fed-in-part FCC operations, for example, resulting in lower overall conversion than the base-line FCC operation.

EXAMPLE VI: Hydrotreating of Algae Oil, Followed by FCC Cracking of Hydrotreated Algae Oil

[0163] Hydrotreatment of the algae oil feed of Example V was performed at various conditions (Runs 4SEBR, 5 SEBR, and 6SEBR) to obtain oil products. These experimental runs were conducted in a semi-batch reactor (continuous flow of H_2 while the oil and catalyst remained in a well-stirred reactor at pressure and temperature). At the end of each 1 hour residence time run, the oil was removed and analyzed as a product sample called "oil product". See the analysis of the three hydrotreated oil products, compared to the algae oil feed (of Tables 4-6), in Tables 14 – 16, below.

[0164] Table 14: % Mass Fraction – Algae Oil Feed and Hydrotreated Samples (4SEBR – 6SEBR)

Sample	FRACTION MASS %					
	Initial – 260 °F	260-400 °F	400-490°F	490-630°F	630-1020°F	1020° F
NS-263-061 Algae Oil Feed	0.0	0.5	1.3	6.6	64.1	27.5
4 SEBR-CFS 4: Hydrotreated, Ni/Mo 370°C, 1000 psi H2	0.0	3.4	7.5	24.3	39.2	25.6
5 SEBR-CFS; Hydrotreated, Ni/Mo 370°C, 15000 psi H2	0.0	4.9	9.6	36.5	36.4	12.6
6 SEBR-CFS 6; Hydrotreated, Ni/Mo 370°C, 1800 psi H2	0.0	3.2	6.9	27.9	38.7	23.3

[0165] Table 15. Compound Classes – Summary for Algae Oil feed and Hydrotreated Samples (4SEBR-6SEBR)

Class	Algae Oil Feed	4SEBR CSF-4	5SEBR CSF-5	6SEBR CSF-6
HC-Saturated	2.0	74.2	75.7	58.1
HC-Unsaturated	9.1	0.9	3.2	5.5
Naphthenes and Aromatics	1.7	3.5	6.5	12.6
N-Aromatics	8.6	0.7	0.2	1.2
Nitriles	0.0	0.0	0.0	0.0
Acid Amides	10.9	0.0	0.0	0.0
Fatty Acids	25.9	0.0	0.0	0.0

Oxygen Compounds	1.3	4.8	2.1	5.6
Sterols	13.6	6.0	1.5	0.1
Sulfur Compounds	0.0	0.0	0.0	1.2
Unknowns	26.9	9.5	10.4	14.0

[0166] Table 16. Elemental Analysis – Algae/Oil Feed and Hydrotreated Samples (4SEBR – 6SEBR)

wt %	Algae Oil Feed	4-SEBR	5-SEBR	6-SEBR
C	77.9	82.9	82.3	85.0
H	10.7	13.1	13.4	14.5
N	3.9	1.5	1.5	0.7
O	6.8	0.5	0.5	0.5
S	0.37	0.70	0.76	0.45

[0167] Three variations of catalytic hydrotreating were conducted at the same temperature (370 degrees C) with the same catalyst, but at three pressures ranging from 1000 psi to 1800 psi. Specifically, 4SEBR, 5SEBR, and 6SEBR were conducted at 1000 psig, 1500 psig, and 1800 psig pressure, respectively. The hydrotreatment catalyst was a commercially-available NiMo/Al2O3 that had been pre-sulfided and handled prior to the semi-batch reaction such that re-oxidation did not occur. The NiMo/Al2O3 catalyst used for these hydrotreating experiments was a sample of catalyst used for processing Canadian oil sands, believed to have a pore structure with BET surface area in the range of 150 – 250 m2/g, micropores in the average diameter range of 50 – 200 Angstroms, and macropores in the range of 1000 – 3000 Angstroms.

[0168] The oil products from Runs 4SEBR, 5SEBR, and 6SEBR were used as feeds for catalytic cracking in the MAT system described above in Example V. The procedures were consistent with those used for the algae oil feed vs. VGO comparison of Example V, allowing comparison of the data from Example V and this Example. The MAT testing, as discussed above, is predictive of commercial FCC performance. Limited oil product sample volume from 5SEBR resulted in limited MAT data for algae oil hydrotreated at 1500 psig.

[0169] Table 17 shows the yield structure in MAT testing of the standard VGO (first column of data) and of the high-severity-hydrotreated oil (6SEBR, second column of data), with the difference calculated and shown in the third data column.

[0170] Table 17. FCC MAT Testing of High-Pressure Hydrotreated Algae Oil compared to Standard VGO Feed

	Yields (wt%)		
	Standard VGO Feed	6SEBR	Difference 6SEBR - VGO
C/O ratio	3.031	2.475	-0.556
Conversion	70.565	70.268	-0.298
Gasoline(C5-421° F)	48.613	44.357	-4.256
Coke yield	4.492	4.932	0.440
LCO yield	15.870	27.392	11.523
LPG yield	15.208	20.117	4.909
H2+C1+C2+H2S	2.076	0.862	-1.214
H2+C1+C2	2.076	0.862	-1.214
T.C3	5.314	6.821	1.507
T.C4	9.894	13.296	3.402
C4=/ Tot. C4's	0.679	0.652	-0.027
C3=/ Tot. C3's	0.856	0.874	0.018
H2	0.211	0.097	-0.114
H2S	0.010	0.000	-0.010
CH4	0.718	0.230	-0.488
C2+	0.587	0.146	-0.441
C2=	0.559	0.388	-0.170
C3+	0.768	0.861	0.093
C3=	4.546	5.961	1.414
iC4+	2.526	3.608	1.082
nC4+	0.655	1.019	0.364
iC4=	2.225	2.752	0.528
nC4=	4.489	5.916	1.427
C4=	6.714	8.669	1.955
C4= =	0.177	0.000	-0.177
DCO	13.565	2.340	-11.225
wt% recovery	97.786	104.828	

[0171] Figure 15 shows the reactivity of the three hydrotreated algae oils, compared to the algae oil feed of Example V and VGO, in the FCC process. The algae oil that had been hydrotreated at higher severity (6SEBR, 1800 psig) showed superior reactivity compared to the algae oils hydrotreated at lower severity (4 and 5SEBR), with the higher-severity-hydrotreated oil being more reactive than the VGO. That is, conversion of the high-severity-hydrotreated algae oil in the MAT test is higher than that for VGO at the same C/O range of about 2 – 2.5. The moderately-hydrotreated oil (5SEBR, 1500 psig) was about as reactive as the VGO, whereas the material produced from hydrotreating at 1000 psi was, very surprisingly, less reactive than the VGO and the crude algae oil feed.

[0172] As shown in Figure 16, hydrotreating improved the coke yields relative to those from the crude algae oil of Example V. The coke yield from the 1800-psig-hydrotreated algae oil was similar to that of the VGO at the same conversion of about 70 wt%.

[0173] The yields from the hydrotreated algae oils in the MAT testing are included in Figures 17 – 22. Product yields are best compared at similar conversions. Therefore, Figures 17 - 22 show weight % yield key products (y-axis) plotted against conversion (x-axis) as obtained by varying C/O. These key yields are discussed in the following paragraph.

[0174] Figure 17 shows that gasoline yields were lower from algae oil feed of Example V and its hydrotreated counterparts (the oil products from 4 – 6SEBR), compared to those from VGO at similar conversions. Figure 18 shows that distillate yields (LCO or “light cycle oil”) were higher from algae oil feed and its hydrotreated counterparts, compared to those from VGO at similar conversions. Figure 19 shows that DCO yields (“decanted oil”, the heaviest and least-valued product from catalytic cracking) were markedly lower for from algae oil feed (crude algae oil) and its hydrotreated counterparts, compared to DCO from the VGO at similar conversions. Figures 20 – 22 show the yields of specific components lighter than gasoline, that is, TC2, TC3, and TC4.

[0175] The yield structure obtained by MAT (FCC) testing of the high-severity-hydrotreated algae oil (6SEBR) suggest the high-severity-hydrotreated algae oil may have a higher value than VGO, even when the cost of the high-pressure hydrotreating is taken into account. The higher distillate yields and reduction in gasoline yields, along with the significant reduction of low-valued DCO, all increase the value of the hydrotreated algae oil. It should be noted that the lower coke-on-FCC-catalyst of the high-severity-hydrotreated algae oil (6SEBR) helps the heat balance in the FCC, which in turn improves conversion and yields.

[0176] Therefore, in certain embodiments, algae oil will be hydrotreated prior to being upgraded in an FCC operation. According to certain embodiments of aromatics and/or hydrogen production disclosure herein, such an FCC operation would be characterized by being loaded-in-part with gallium-cation-catalyst and fed-in-part with algae-oil. Improved coke yields vs conversion for the hydrotreated algae oil may affect the optimum catalyst and algae oil percentages, but the gallium catalyst and algae oil percentages described above (for example, 1 – 20 wt%, or 5 – 10 wt%) are expected to be reasonable starting places for optimization of the hydrotreated algae oil FCC embodiments.

[1077] Therefore, certain methods of upgrading algae oil may comprise:

a) obtaining a crude algae oil from algae biomass, the crude algae oil being a full boiling range algae oil comprising material in the boiling range of distillate (about 400 – 630 degrees F) and in the boiling range of gas oil (about 630 – 1020 degrees F) and in the boiling range of vacuum bottoms (about 1020 degrees F+), wherein the total of the distillate plus gas oil boiling range material is at least 55 wt%, and wherein certain embodiments of this crude algae oil may be obtained, for example, from any of the HTT hydrothermal-treatment and solvent extraction methods described earlier in this document;
b) hydrotreating the crude algae oil over one or more hydrotreating catalysts adapted for hydrotreatment of fossil petroleum resid/bitumen (including oil/bitumen from oil sands or tar sands), and/or over one more hydrotreating catalysts having a pore structure including macro-pores and characterized by BET surface areas in the range of 150 – 250 m2/g, micropores in the average diameter range of 50 – 200 Angstroms, and macropores in the range of 1000 – 3000 Angstroms, wherein said one or more hydrotreating catalysts may comprise Ni/Mo and/or Co/Mo on alumina or silica-alumina supports having said pore structure;
c) wherein the hydrotreating conditions are in the ranges of: 1000 – 2000 psig (and more typically 1500 – 2000 psig, about 0.8 – 1.5 1/hr LHSV (more typically about 1 1/hr LHSV), 300 – 425 degrees C (more typically 350 – 400 degrees C), with typical gas/oil ratios being at least 2000 scf/b;

d) separating, by conventional separation vessels/methods, the liquid hydrotreated oil from the hydrotreater effluent, typically meaning separating the liquid hydrotreated oil from hydrogen and gasses; and

e) sending the liquid hydrotreated oil or fractions thereof to a processing unit that is an FCC unit comprising at least some gallium-modified catalyst selected from any of the gallium-catalyst embodiments described in this disclosure, for example, at least some gallium-cation catalyst.

[0178] Certain alternative embodiments may comprise step (b) instead being: hydrotreating the crude algae oil over one or more hydrotreating catalysts characterized by BET surface areas in the range of about 150 – 250 m2/g, and comprising macropores of at least 1000 Angstroms, wherein said one or more hydrotreating catalysts may comprise Ni/Mo and/or Co/Mo on alumina or silica-alumina supports having said pore structure. Certain alternative embodiments may comprise step (b) instead being: hydrotreating the crude algae oil over one or more hydrotreating catalysts comprising macropores in the range of at least about 1000 Angstroms. End products from the above processes of this Example may include one or more of BTX plant feedstock, gasoline, kerosene, jet fuel, diesel fuel, or lube base stock, for example. Certain methods of this Example may comprise, consist essentially of, or consist of method steps a-e above. Algae oils/fractions may range from very little to all of the feedstock for the processing unit(s) in steps b and e above, for example, from about 0.1 volume percent up to 100 volume percent of the liquid feedstock being fed to said processing unit(s). In many embodiments of step e above, however, the hydrotreated oil derived from the crude algae oil will be a minor portion of the entire FCC feedstock (for example, 1 – 20 wt% or 5 – 10 wt%) and the gallium-cation catalyst will be only a portion of the entire FCC catalyst loading (for example, 1 – 20 wt% or 5 – 10 wt%).

EXAMPLE VII: Thermal-Treatment of Algae Oil, Followed by Hydrotreating and FCC Cracking of Hydrotreated Algae Oil

[0179] Certain crude algae oils may be thermally treated prior to being fed to FCC operations such as described in Example VI. Because of the complex composition and/or the high molecular weight materials of said certain algae oils extracted from biomass, thermal treatment prior to processing in any catalytic unit may be effective in reducing one or more of the following characteristics: oxygen content and/or other heteroatom content, metals content, high molecular weight content, 1000 degree F+ content, 1020 degree F+ content, boiling range/distribution, viscosity, and/or catalyst poisons and/or coke-on-catalyst precursors. In certain embodiments, several of these characteristics are expected to be related to catalyst deactivation due to poisoning of catalyst active sites (such as acidic sites being poisoned by basic nitrogen compounds) and/or producing coke-on-catalyst. In certain embodiments, thermal treatment will reduce most or all of these characteristics.

[0180] Therefore, thermal treatment of whole crude algae oil obtained from biomass is expected to mitigate catalyst deactivation and/or coke-on-catalyst production caused by the crude algae oil, thereby extending catalyst life in such units as a hydrotreater, or improving heat balances in continuous catalyst regeneration systems such as FCC units. The thermal treatment methods of this Example may be used in conjunction with hydrotreating over large-pore catalysts (see Example VI) to improve catalyst lives and/or heat balances in downstream units.

[0181] In this Example, therefore, a thermal treatment method may be applied to certain crude algae oils, the method comprising:

a) obtaining a crude algae oil from algae biomass (for example, by any of the HTT processes described above), the crude algae oil being a full boiling range algae oil comprising material in the boiling range of distillate (about 400 – 630 degrees F) and in the boiling range of gas oil (about 630 – 1020 degrees F) and in the boiling range of vacuum bottoms (about 1020 degrees F+), wherein the total of the distillate plus gas oil boiling range material is at least 55 wt%;

b) thermally treating the crude algae oil (the whole crude algae oil) by heating the crude algae oil to a temperature in the range of 300 – 450 degrees C, with or without added gas or diluent(s), at a pressure in the range of 0 – 1000 psig (and more typically 0 – 300 psig), and holding the algae oil at that temperature for a period of 0 minutes to 8 hours, and more typically 0.25 – 8 hours or 0.5 – 2 hours;

c) separating, by conventional separation vessels/methods, liquid thermally-treated oil from the thermal treatment effluent, typically meaning separating the liquid thermally-treated oil from hydrogen and gasses and from coke/solids; and

d) hydrotreating the thermal treatment effluent over one or more hydrotreating catalysts adapted for hydrotreatment of fossil petroleum resid/bitumen (including oil/bitumen from oil sands or tar sands), and/or over one more hydrotreating catalysts having a pore structure including macro-pores and characterized by BET surface areas in the range of 150 – 250 m2/g, micropores in the average diameter range of 50 – 200 Angstroms, and macropores in the range of 1000 – 3000 Angstroms, wherein said one or more hydrotreating catalysts may comprise Ni/Mo and/or Co/Mo on alumina or silica-alumina supports having said pore structure;
e) wherein the hydrotreating conditions are in the ranges of: 1000 – 2000 psig (and more typically 1500 – 2000 psig, about 0.8 – 1.5 1/hr LHSV (more typically about 1 1/hr LHSV), 300 – 425 degrees C (more typically 350 – 400 degrees C), with typical gas/oil ratios being at least 2000 scf/b;
f) separating, by conventional separation vessels/methods, the liquid hydrotreated oil from the hydrotreater effluent, typically meaning separating the liquid hydrotreated oil from hydrogen and gasses; and
g) sending the liquid hydrotreated oil or fractions thereof to a processing unit that is an FCC unit comprising at least some gallium-modified catalyst selected from any of the gallium-catalyst embodiments described in this disclosure, for example, at least some gallium-cation catalyst.

[0182] End products from the above process may include one or more of BTX plant feedstock, gasoline, kerosene, jet fuel, diesel fuel, or lube base stock, for example. Certain methods of this Example may comprise, consist essentially of, or consist of method steps a-g above. Algae oils/fractions may range from very little to all of the feedstock for the processing unit(s) in steps b, d, and g above, for example, from about 0.1 volume percent up to 100 volume percent of the liquid feedstock being fed to said processing unit(s). In many embodiments of step g above, however, the hydrotreated oil derived from the crude algae oil will be only a portion of the entire FCC feedstock (for example, 1 – 20 wt% or 5 – 10 wt%) and the gallium-modified catalyst will be only a portion of the entire FCC catalyst loading (for example, 1 – 20 wt% or 5 – 10 wt%).

[0183] In alternative embodiments, the above steps of this Example may be modified so that only a portion of the crude algae oil, such as a heavy fraction, is thermally-treated, but both the thermally-treated portion (minus any solids/coke and gasses formed in the thermal treating) and the un-thermally-treated portion of the crude algae oil are combined for hydrotreating and subsequent fluid catalytic cracking.

Example VIII: Fluidized Bed Process Unit Commercial Application

[0184] Certain embodiments may comprise “spiking” relatively small amounts of renewable oil(s) into a refinery unit previously operating on non-renewable feedstocks, and providing at least some gallium-cation catalyst in the unit. For example, by “relatively small amounts” may be meant that the renewable oil may be added as 1 – 20 wt% (more typically 5 – 10 wt%) of a unit’s feedstock, with gallium-cation catalyst being added as 1 – 20 wt% (more typically 5 – 10 wt%) of the unit’s catalyst. Such a “spiking” approach may be particularly effective in an fluidized catalyst process unit, for example, an FCC unit, as further described below.

[0185] As schematically illustrated in Figure 23, conventional FCC feedstock is heated and sprayed into the base of a riser (a vertical or upward-sloped pipe), where the pre-heated feedstock contacts fluidized zeolite catalyst typically at about 950 to 1030 degree F. (approximately 510 to 555 degree C.). The hot catalyst vaporizes the feedstock and catalyzes the cracking reactions that break down the high molecular weight hydrocarbons into lighter components including LPG (liquid petroleum gas such as C3-C4 olefins), and acyclic or cyclic hydrocarbons (C5-C12). The catalyst-hydrocarbon mixture flows upward through the riser for just a few seconds (for example, 2-4 seconds) and then the mixture is separated via cyclones. The catalyst-free hydrocarbons are routed to a fractionation column for separating shorter hydrocarbon products (for example, C3-C12 hydrocarbons) from the heavier fuels. The shorter hydrocarbons, many of which are suitable as gasoline products, are more volatile than the heavier fuels. The heavier fuels include diesels and jet fuels that fractionally distill between approximately 200 degree C and 350 degree C. at atmospheric pressure.

[0186] During the trip up the riser, the cracking catalyst is "spent" by reactions that deposit coke on the catalyst and greatly reduce activity and selectivity. The process of coke formation is important to the overall process because it increases the H/C (hydrogen to carbon) ratio of the gaseous products to a range more suitable for gasoline. The spent catalyst is disengaged from the cracked hydrocarbon vapors and sent to a stripper where it is contacted with steam to remove hydrocarbons remaining in the catalyst pores. The spent catalyst then flows into a fluidized-bed regenerator where air (or in some cases air plus oxygen) is used to burn off the coke to restore catalyst activity and also provide the necessary heat for the next reaction cycle. The regenerated catalyst then flows to the base of the riser, repeating the cycle.

[0187] Catalyst and additives are typically added to FCC units using systems each comprising a bin and a lock hopper. The minimum catalyst addition rates are determined by the physical attrition and loss of the FCC catalyst as fines that escape capture in the cyclone systems in both the regenerator flue gas and the oil that goes from the riser/reactor to the main fractionators. Thus, catalyst fines show up in the slurry oil that is also sometimes called decant oil or DCO. Catalyst/additives are added to the FCC at rates above this physical loss depending on the activity for conversion and yields that are desired in the FCC. For example, if a higher activity of catalyst/additive is required, fresh catalyst/additive will be added at a higher rate. Because this rate exceeds the physical loss of catalyst/additive, some catalyst in the unit (the “inventory” of equilibrium catalyst/additive) will need to be removed to maintain the inventory of catalysts/additive constant. The inventory of catalyst in the unit is often called “equilibrium” catalyst/additive because it comprises catalyst/additive of various ages and activities due to its being added over time into the unit. This removal of inventory (equilibrium catalyst/additive), like the addition, is done with bins and a lock hopper system with the ability to pneumatically carry the catalyst/additives from the regenerator to eventual disposal. Both the FCC catalyst and additive systems are based on the same principles, but are mechanically separate systems so their addition rates can be independently varied for optimization of both and therefore the system as a whole.

[0188] The modifications to such a conventional FCC cracking process to include aromatics production from the renewable oils according to this invention are expected to be minimal when the renewable oil(s) and gallium-cation catalyst are in the 1 – 20 wt% or 5 – 10 wt% ranges as discussed earlier in this document. Conventional FCC cracking catalyst would be maintained as the majority component of the catalyst contained in the unit, for example, as 80 – 99 wt% or 90 – 95 wt% of the catalyst (when gallium-cation catalyst is provided as 1-20 wt% or 5 – 10 wt%, respectively). The gallium-cation catalyst would be added or removed as desired by means of the additive bin and lock hopper system described above. However, some modifications in contact time, temperature and/or catalyst to oil ratios, for example, may be made. While it may be desirable to lower FCC catalyst-contact temperature, in view of the gallium-cation catalyst in the Examples exhibiting its optimum performance at approximately 400 degrees C, it may not be possible to do this in view of most FCC operations on gas oil and/or heavy gas oil requiring 510 – 555 degrees C.

Example IX: Purpose-Built Process Unit Commercial Application

[0189] In certain embodiments, a refinery unit may be purpose-built for processing solely renewable oil(s) over catalyst that is only, or substantially, a gallium-cation catalyst, to produce excellent yields of BTEX and/or gasoline and hydrogen. One such purpose-built unit may be similar to a UOP Cyclar ™ unit, which comprises a moving bed of said gallium-cation catalyst and a coke-burning regeneration section, as schematically portrayed in Figure 24. Or, for example, a purpose-built fixed-bed reactor unit may be effective. Regeneration in both units may be limited to solely coke-burning followed by reduction during normal operation in the reactor.

[0190] Both units would be optimized with respect to temperature, pressure, flowrates, gallium loading, etc., as would be understood by those of skill in the art. In certain embodiments of a packed mode configuration at WHSV = 1.0, the reactor would be operated at 350 – 450 degrees C, and more preferably at about 400 degrees C. Other contacting configurations and conditions may yield optimum temperatures of 450 – 500°C, especially with WHSV > 1.0. These purpose-built units would preferably operate on 80 - 100 wt %, and more preferably 90 – 100 wt% renewable oil(s), for example, algae oil, with the catalyst being 80-100 wt%, or more preferably, 90 – 100 wt%, gallium-cation-retaining catalyst. Information regarding conventional UOP Cyclar ™ units may be obtained from UOP, Des Plaines, Illinois, U.S.A. Information regarding fixed-bed reactor units may be obtained from several petroleum refinery unit design companies.

[0191] It may be noted from the above detailed description, including Example I – IX, that many embodiments may be described as a process for producing BTEX or gasoline, the process comprising: contacting, at elevated temperature, a feedstock comprising at least one renewable oil with a catalyst comprising a catalytically-active form of gallium to produce a product stream comprising BTEX. The renewable oil may be canola oil, algae oil, algae oil extracted from a green alga or a blue-green alga, or other renewable oil(s), or fractions thereof, for example. It may be noted from the data herein that certain embodiments of the process the renewable oil is canola oil, that BTEX may be in said product stream in a yield of greater than 35 wt-%. It may be noted from the data herein that certain embodiments of the process the renewable oil is algae oil, that BTEX may be in said product stream in a yield of greater than 42 wt-%. In certain of these embodiments, said product stream comprises a yield of greater than 15% wt-% Benzene. Said catalyst may a zeolitic catalyst that is gallium-modified to comprise gallium cations in a ratio of about 1/1 Ga/framework-Al, for example. Said contacting may done in many reactors/vessels/risers, for example: in a single reactor, a series of reactors, a series of at least a first reactor and a second reactor, wherein liquid is removed from the intermediate product stream between the first and second reactors, and vapor from the first reactor is fed to said second reactor, a fixed-bed reactor, in a moving catalyst bed, and/or a riser of a fluidized catalytic cracking unit, for example. In certain embodiments of contact taking place in a riser, the contacting may take place at 510 to 555 degree C temperature or at 400 – 555 degrees C temperature, for example. Said contacting may take place for 2 – 4 seconds. In certain embodiments, said renewable oil is algae oil that has not been processed between being extracted from algae and said contacting. In certain embodiments, said algae oil has been processed in a RBD process and/or a degumming process, but in certain embodiments the algae oil has not been processed in a RBD process and/or a degumming process. In certain embodiments said algae oil has been hydrotreated prior to said contacting. In certain embodiments, the catalyst may be a gallium-doped form of one or more zeolite-alumina matrix catalysts with pore sizes having 10 oxygen atoms in the pore mouth, for example, selected from the group consisting of: ZSM-5, ZSM-11, ZSM-23, MCM-70, SSZ-44, SSZ-58, SSZ-35, and ZSM-22. Certain embodiments may be described as: a process for producing aromatics (for BTEX feedstocks or for gasoline, for example) and/or hydrogen from renewable oil, the process comprising: providing a reactor vessel or riser containing catalyst, said catalyst comprising a gallium-cation catalyst; and contacting a feedstsock with said catalyst at elevated temperature; wherein said feedstock comprises renewable oil selected from the group consisting of: oil derived from biomass living in the past 50 years; canola oil; oils extracted from vegetables including corn, soybean, sunflower, and sorghum; algae oil from naturally-occurring algae; algae oil from genetically modified algae; oil from seeds; oil from fungi; and oil from a photosynthetic or non-photosynthetic bacteria. Said renewable oil may be various percentage of the entire feedstock to these various processes, for example, in the range of about 1 wt% (or even less, for example, 0.01 wt %) up to 100 wt% of said feedstock. For example, said renewable oil may 1 – 20 wt%, 50 – 100 wt%, 80 - 100 wt% of said feedstock, or 90 - 100 wt% of the total feedstock. The catalyst comprising a catalytically-active form of gallium and/or the gallium-cation catalyst mentioned above may, in certain embodiments, comprise any percentage of the total catalyst of the process, for example 1 wt% (or even less, for example, 0.01 wt%) up to 100 wt% of said feedstock. For example, the catalyst comprising a catalytically-active form of gallium and/or the gallium-cation catalyst may be 1 – 20 wt%, 50 – 100 wt%, 80 – 100 wt%, or 90 – 100 wt% of said feedstock. In some embodiments, the weight percentage of catalyst comprising a catalytically-active form of gallium and/or the gallium-cation catalyst in the reactor vessel or riser will be equal to the weight percentage of renewable oil in the feedstock to the process. In certain embodiments, the riser is a fluidized catalytic cracking unit (FCC) riser and the catalyst further comprises a Y-Zeolite FCC catalyst in said riser, so that the FCC operates on catalyst/additives comprising catalyst comprising catalytically-active form of gallium and/or the gallium-cation catalyst, Y-zeolite, and optionally other conventional FCC additives. In certain embodiments, the reactor vessel is a moving-bed vessel adapted so that said catalyst moves through the reactor vessel by gravity. In certain embodiments, the temperature of contact with the catalyst is an elevated temperature is in the ranges of 375 – 425 degrees C or 350 – 555 degrees C, but in other embodiments, it may be different from these ranges based on the requirements of catalysts with which the gallium catalyst is mixed. Of particular interest in certain embodiments are renewable oil(s) obtained from non-vascular photosynthetic organism(s), for example, naturally-occurring algae or cyanobacteria, or genetically-modified algae or cyanobacteria. In certain embodiments, the renewable oil mixed or otherwise combined with other components that are selected from the group consisting of: one or more fossil oil fractions, one or more refined fossil oil products or fractions, naphtha, gasoline, jet fuel, diesel, and any combination thereof. Certain embodiments of the invention may comprise any renewable oil product made by an upgrading process comprising any of the processes described above, for example, a BTEX-rich stream for a petrochemical plant or other uses, or gasoline and/or other fuels.

[0192] In the this Description, ranges of temperature, holding time/residence time/LHSV, gas to oil ratios, BET surface in m2/g, pore sizes in Angstroms, pressure in psig, and/or other ranges of variables, are given for many embodiments of the invention. It should be understood that the ranges are intended to include all sub-ranges, and to include each incremental amount of temperature, holding time/residence time/LHSV, gas to oil ratios, BET surface in m2/g, pore sizes in Angstroms, pressure in psig, and other variable, within each broad range given. For example, while a broad range of pressure of 1000 – 2000 psig is mentioned, certain embodiments may include any of the following sub-ranges or any pressure within any of the following sub-ranges: 1000 – 1050, 1050 – 1100, 1100 – 1150, 1150 – 1200, 1200 – 1250, 1250 – 1300, 1300 – 1350, 1350 – 1400, 1400 – 1450, 1450 – 1500, 1500 – 1550, 1550 – 1600, 1600 – 1650, 1650 – 1700, 1700 – 1750, 1750 – 1800, 1800 – 1850, 1850 – 1900, 1900 – 1950, and 1950 – 2000 psig. For example, while broad ranges of 300 – 425, 300 – 450, and 350 - 555 degrees C are mentioned, certain embodiments may include any temperature within any of these ranges, or any 10 degrees C sub-ranges, for example. Examples of 10 degrees sub-ranges for the range of 300 – 450 degrees C are: 300 – 310, 310 – 320, 320 – 330, 330 – 340, 340 – 350, 350 – 360, 360- 370, 370 – 380, 380 – 390, 390 – 400, 400 – 410, 410 – 420, 420 – 430, 430 – 440, 440 – 450 degrees C. Examples of 10 degrees sub-ranges for the range of 350 – 555 degrees C are: 350 – 360, 360 – 370, 370 – 380, 380 – 390, 390 – 400, 400 – 410, 410 – 420, 420 – 430, 430 – 440, 440 – 450, 450 – 460, 460 – 470, 470 – 480, 480-490, 490 – 500, 500 – 510, 510 – 520, 520 – 530, 530 – 540, 540 – 550, and 545 – 555 degrees C.

[0193] Also included this disclosure, wherein values such as degrees, mass percent or weight percent are written or shown in Tables or Figures, are those values but with “about” inserted before each value, as one of average skill in the art will understand that “about” these values may be appropriate in certain embodiments of this disclosure.

[0194] While certain embodiments have been shown and described herein, it will be obvious to those skilled in the art that such embodiments are provided by way of example only. Numerous variations, changes, and substitutions will now occur to those skilled in the art without departing from the disclosure. It should be understood that various alternatives to the embodiments specifically described herein may be employed in practicing the invention, and that the invention extends to all equivalents within the scope of the following claims.

CLAIMS

1. A process for producing BTEX or gasoline, the process comprising:
contacting, at elevated temperature, a feedstock comprising at least one renewable oil with a catalyst comprising a catalytically-active form of gallium to produce a product stream comprising BTEX.

2. A process as in Claim 1, wherein said renewable oil is canola oil.

3. A process as in Claim 2, wherein BTEX is in said product stream in a yield of greater than 35 wt-%.

4. A process as in Claim 1, wherein said renewable oil is algae oil.

5. A process as in Claim 4, wherein said renewable oil is crude algae oil extracted from a green alga or a blue-green alga.

6. A process as in Claim 4, wherein BTEX is in said product stream in a yield of greater than 42 wt-%.

7. A process as in Claim 3, wherein said product stream comprises a yield of greater than 15% wt-% Benzene.

8. A process as in Claim 6, wherein said product stream comprises a yield of greater than 15% wt-% Benzene.

9. A process as in any one of Claims 1-8, wherein said catalyst is a zeolitic catalyst that is gallium-modified to comprise gallium cations in a ratio of about 1/1 Ga/framework-Al.

10. A process as in any one of Claims 1 -8, wherein said contacting is done in a single reactor.

11. A process as in any one of Claims 1 -8, wherein said contacting is done in a series of at least a first reactor and a second reactor, wherein liquid is removed from the intermediate product stream between the first and second reactors, and vapor from the first reactor is fed to said second reactor.

12. A process as in any one of Claims 1-8, wherein said contacting is done in a fixed-bed reactor.

13. A process as in any one of Claims 1-8, wherein said contacting is done in a moving catalyst bed.

14. A process as in any one of Claims 1 -8, wherein said contacting is done in a riser of a fluidized catalytic cracking unit.

15. A process as in Claim 14, wherein said contacting is done at 510 to 555 degree C temperature.

16. A process as in Claim 14, wherein said contacting is done at 400 – 555 degrees C temperature.

17. A process as in Claim 14, wherein said contacting is done for 2 – 4 seconds.

18. A process as in any of Claims 1, 4 - 6, and 8, wherein said renewable oil is algae oil that has not been processed between being extracted from algae and said contacting.

19. A process as in any one of Claims 1, 4 – 6, and 8, wherein said algae oil has been processed in a RBD process and/or a degumming process.

20. A process as in any one of Claims 1, 4 – 6, and 8, wherein said algae oil has not been processed in a RBD process and/or a degumming process.

21. A process as in any one of Claims 1, 4 – 6, and 8, wherein said algae oil has been hydrotreated prior to said contacting.

22. A process as in any one of Claims 1-21, wherein said renewable oil is 1 – 100 wt% of said feedstock.

23. A process as in any one of Claims 1 – 21, wherein said renewable oil is 1 – 20 wt% of said feedstock.

24. A process as in any one of Claims 1 – 21, wherein said renewable oil is 80 - 100 wt% of said feedstock.

25. A process as in any one of Claims 1 – 21, wherein said renewable oil is 90 - 100 wt% of said feedstock.

26. A process as in any one of Claims 1 - 21, wherein the catalyst is a gallium-doped form of one or more zeolite-alumina matrix catalysts with pore sizes having 10 oxygen atoms in the pore mouth.

27. A process as in Claim 26, wherein said catalyst is a gallium-doped form of a zeolitic catalyst selected from the group consisting of: ZSM-5, ZSM-11, ZSM-23, MCM-70, SSZ-44, SSZ-58, SSZ-35, and ZSM-22.

28. A process for producing BTEX aromatics and/or hydrogen from renewable oil, the process comprising:

providing a reactor vessel or riser containing catalyst, said catalyst comprising a gallium-cation catalyst; and

contacting a feedstsock with said catalyst at elevated temperature;

wherein said feedstock comprises renewable oil selected from the group consisting of: oil derived from biomass living in the past 50 years; canola oil; oils extracted from vegetables including corn, soybean, sunflower, and sorghum; algae oil from naturally-occurring algae; algae oil from genetically modified algae; oil from seeds; oil from fungi; and oil from a photosynthetic or non-photosynthetic bacteria.

29. A process as in Claim 28, wherein said renewable oil is 1 – 100 wt% of said feedstock, and said gallium-cation catalyst is 1 – 100 wt% of said catalyst in the reactor vessel or riser.

30. A process as in Claim 28, wherein said renewable oil is 1 – 20 wt% of said feedstock, and said gallium-cation catalyst is 1 - 20 wt% of said catalyst in the reactor vessel or riser.

31. A process as in Claim 28, wherein said renewable oil is 80 – 100 wt% of said feedstock, and said gallium-cation catalyst is 80 – 100 wt% of said catalyst in the reactor vessel or riser.

32. A process as in Claim 28, wherein said renewable oil is 90 – 100 wt% of said feedstock, and said gallium-cation catalyst is 90 – 100 wt% of said catalyst in the reactor vessel or riser.

33. A process as in Claim 28, wherein said the weight percentage of gallium-cation catalyst in the reactor vessel or riser is equal to the weight percentage of renewable oil in the feedstock.

34. A process as in any one of Claims 28-33, wherein said riser is a fluidized catalytic cracking unit (FCC) riser.

35. A process as in Claim 34, wherein said catalyst further comprises a Y-Zeolite FCC catalyst in said riser.

36. A process as in any one of Claims 28– 33, wherein said reactor vessel is a moving-bed vessel adapted so that said catalyst moves through the reactor vessel by gravity.

37. A process as in any one of Claims 28 - 33, wherein said reactor vessel is a fixed-bed reactor.

38. A process as in any one of Claims 28 - 33, wherein said elevated temperature is in the range of 375 – 425 degrees C.

39. A process as in any one of Claims 28 – 33 wherein said elevated temperature is in the range of 350 – 555 degrees C.

40. A process for producing BTEX aromatics or gasoline from a renewable oil obtained from a non-vascular photosynthetic organism, the process comprising contacting a feedstock comprising said renewable oil at elevated temperature with a catalyst that retains gallium in a catalytically-active form.

41. A process as in Claim 40, wherein said catalyst is a gallium-doped form of one or more zeolite-alumina matrix catalysts with pore sizes having 10 oxygen atoms in the pore mouth.

42. A process as in Claim 40, wherein said catalyst is a gallium-doped form of a zeolitic catalyst selected from the group consisting of: ZSM-5, ZSM-11, ZSM-23, MCM-70, SSZ-44, SSZ-58, SSZ-35, and ZSM-22.

43. A process as in Claim 40, wherein said catalyst comprises gallium cations.

44. A process as in Claim 40, wherein said elevated temperature is in the range of 350 - 555 degree C.

45. A process as in Claim 40, wherein said elevated temperature is in the range of 375 – 425 degrees C.

46. A process as in Claim 40, wherein said feedstock is 100% oil obtained from a non-vascular photosynthetic organism.

47. A process as in Claim 40 wherein said feedstock is 90 – 100% oil obtained from a non-vascular photosynthetic organism.

48. A process as in Claim 40, wherein said feedstock is 80 – 100% oil obtained from a non-vascular photosynthetic organism.

49. A process as in Claim 40, wherein said feedstock is 50 – 100% oil obtained from a non-vascular photosynthetic organism.

50. A process as in Claim 39, wherein said feedstock is 1 – 20 wt% oil obtained from a non-vascular photosynthetic organism.

51. A process as in any one of Claims 46 - 50, wherein said oil obtained from a non-vascular photosynthetic organism is extracted from naturally-occurring algae or cyanobacteria.

52. A process as in any one of Claims 46 - 50, wherein said oil obtained from a non-vascular photosynthetic organism is extracted from genetically-modified algae or cyanobacteria.

53. A process as in any one of Claims 47 - 52, wherein the remainder of the feedstock that is not oil obtained from a non-vascular photosynthetic organism is selected from the group

consisting of: one or more fossil oil fractions, one or more refined fossil oil products or fractions, naphtha, gasoline, jet fuel, diesel, and any combination thereof.

54. A renewable oil product made by a process comprising any of the processes of Claims 1 – 53.

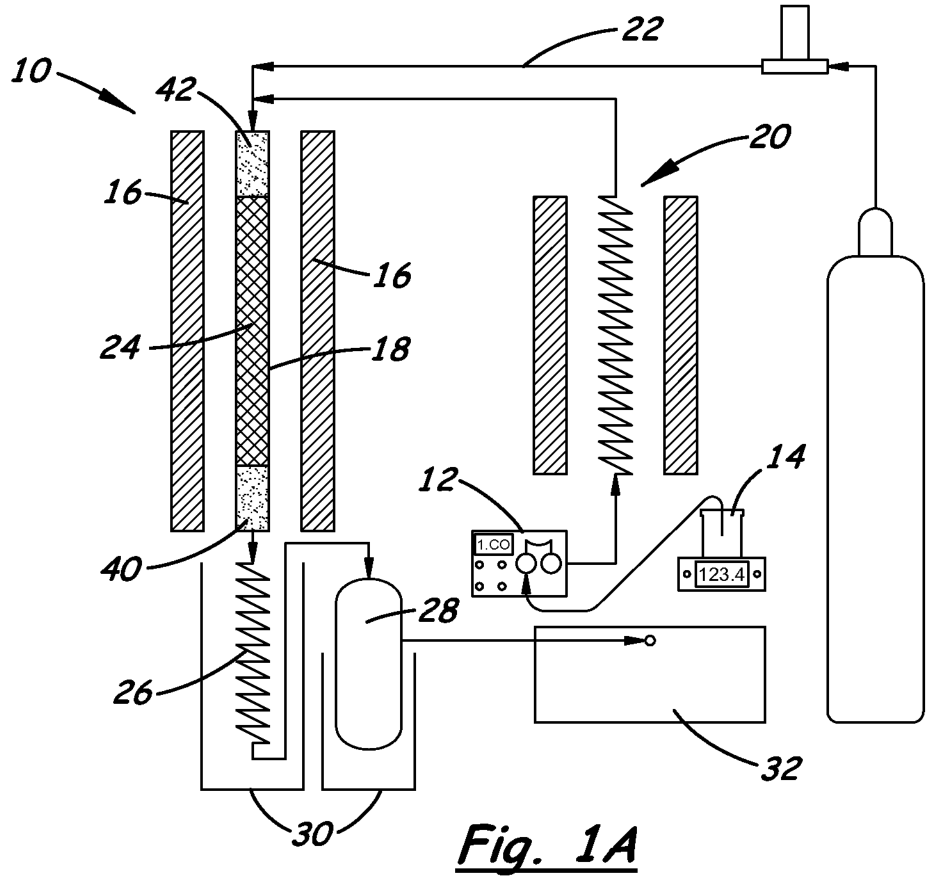
10
42
22
20
16
16
24
18
12
1.CO
14
123.4
40
28
26
32
30

Fig. 1A

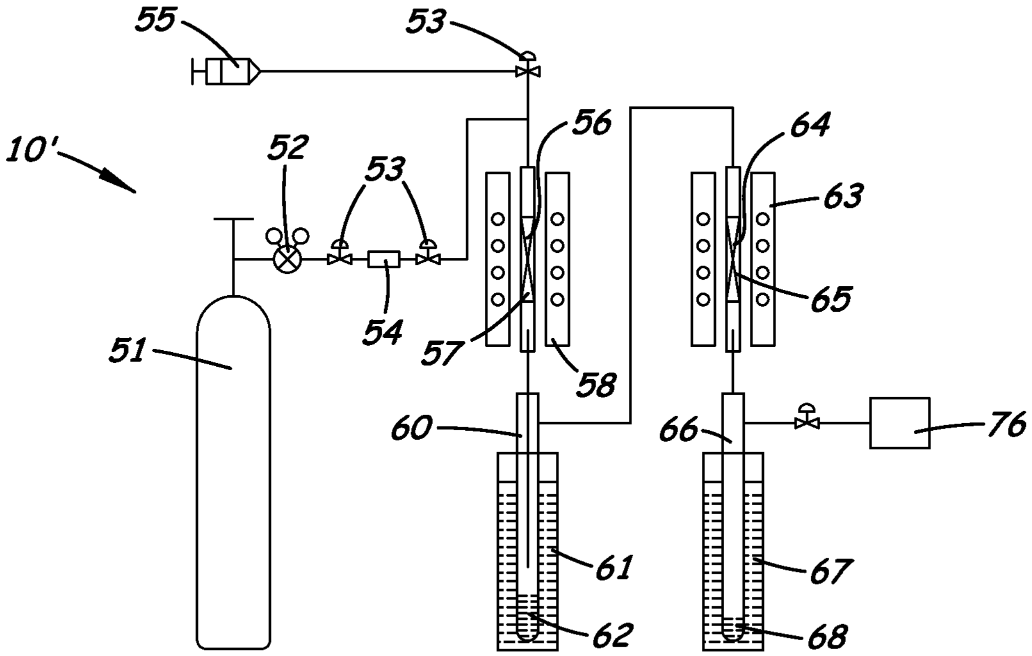
55
53
10'
52
53
56
64
63
54
51
57
58
65
60
66
76
61
67
62
68

Fig. 1B

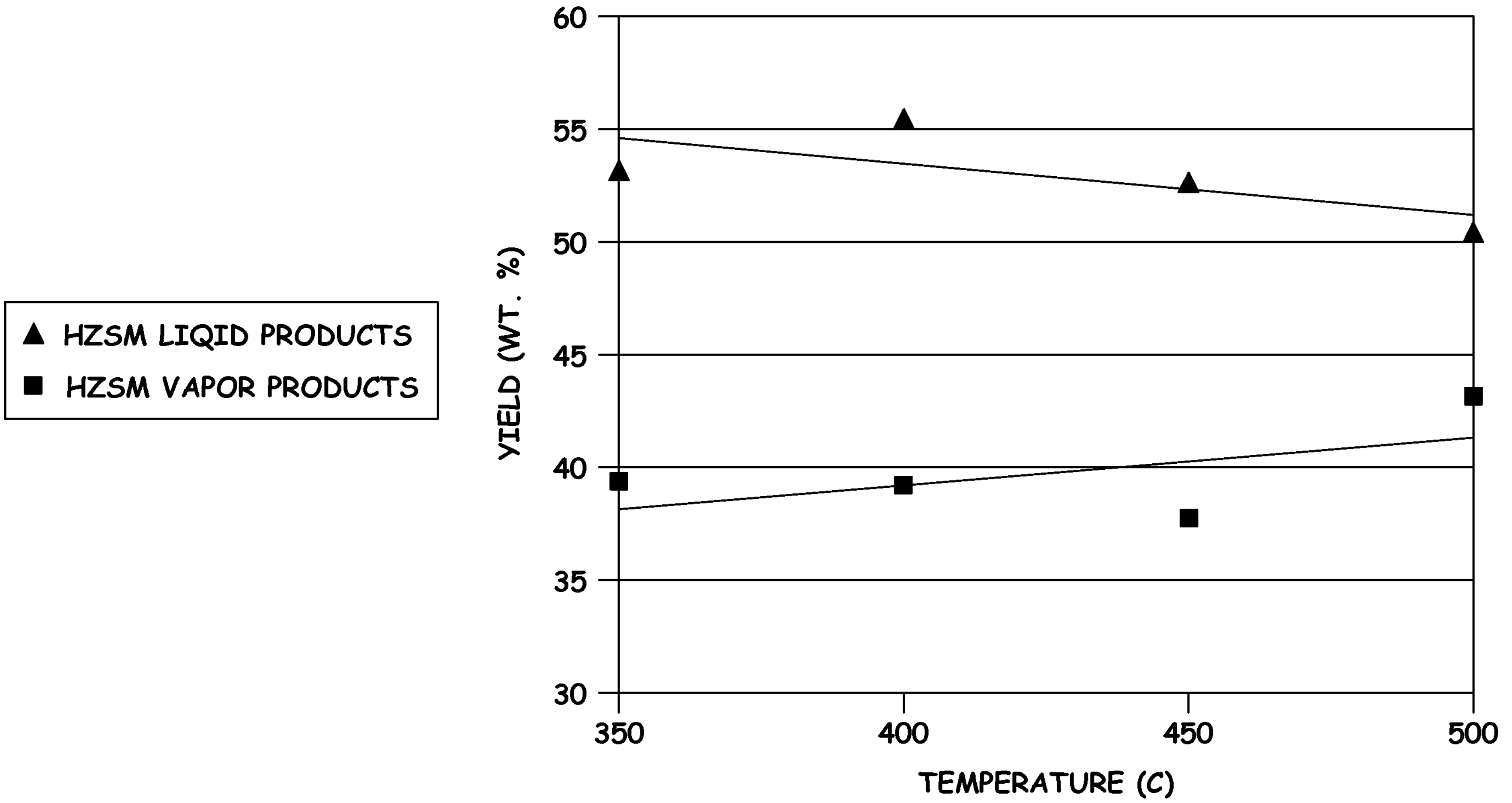

Fig. 2

(CANOLA OIL)

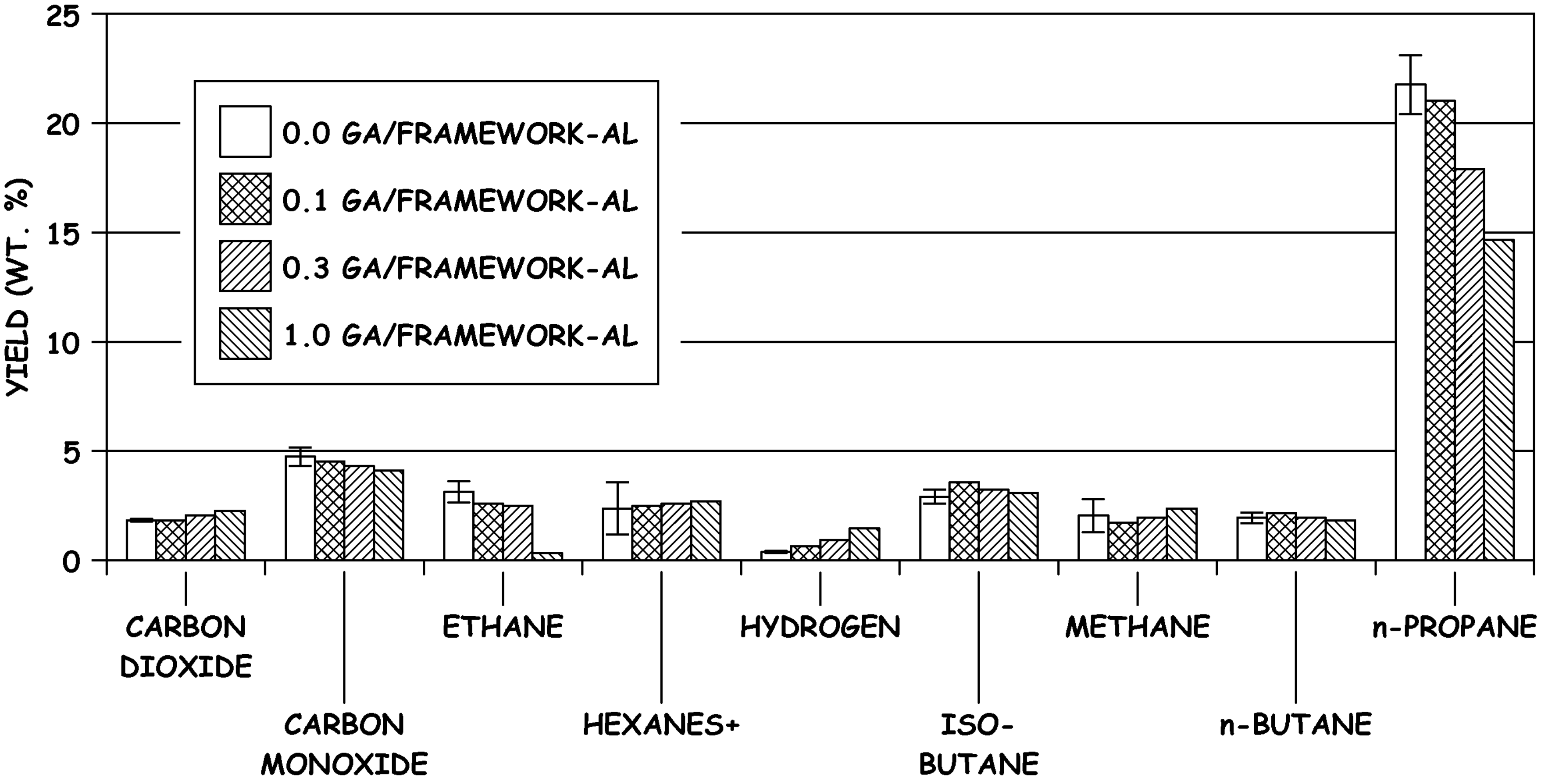

Fig. 3
(CANOLA OIL)

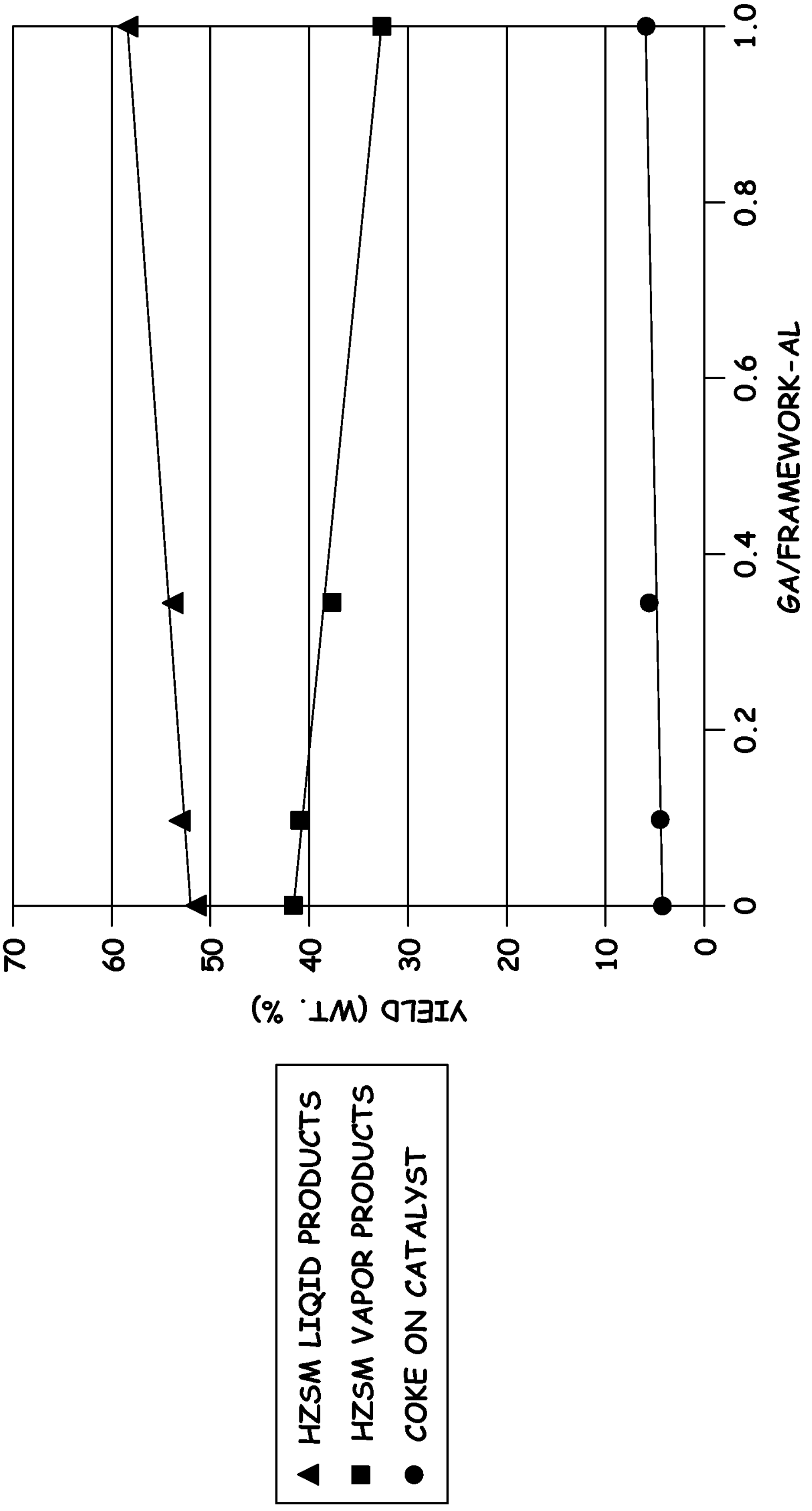

Fig. 4
(CANOLA OIL)

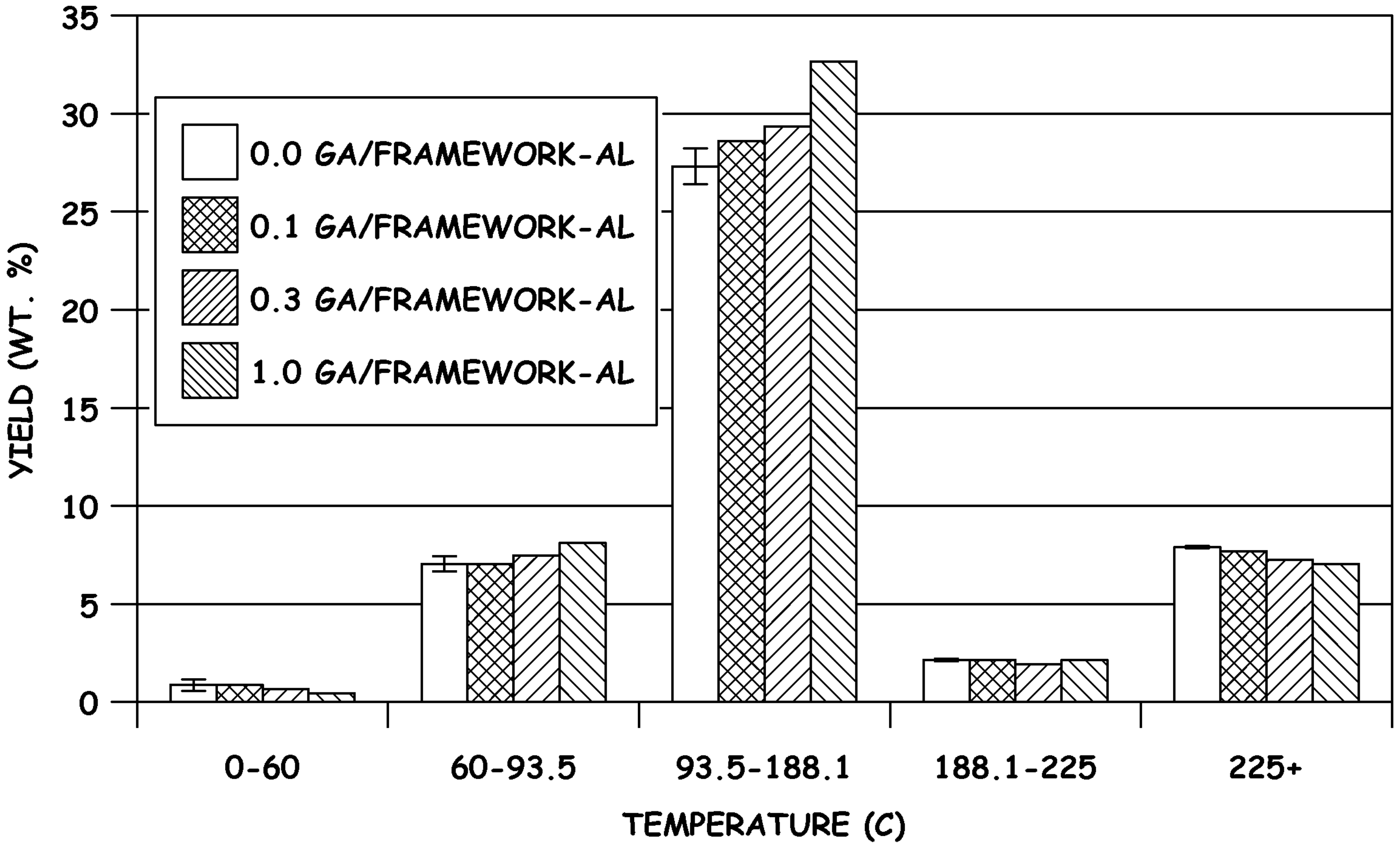

Fig. 5

(CANOLA OIL)

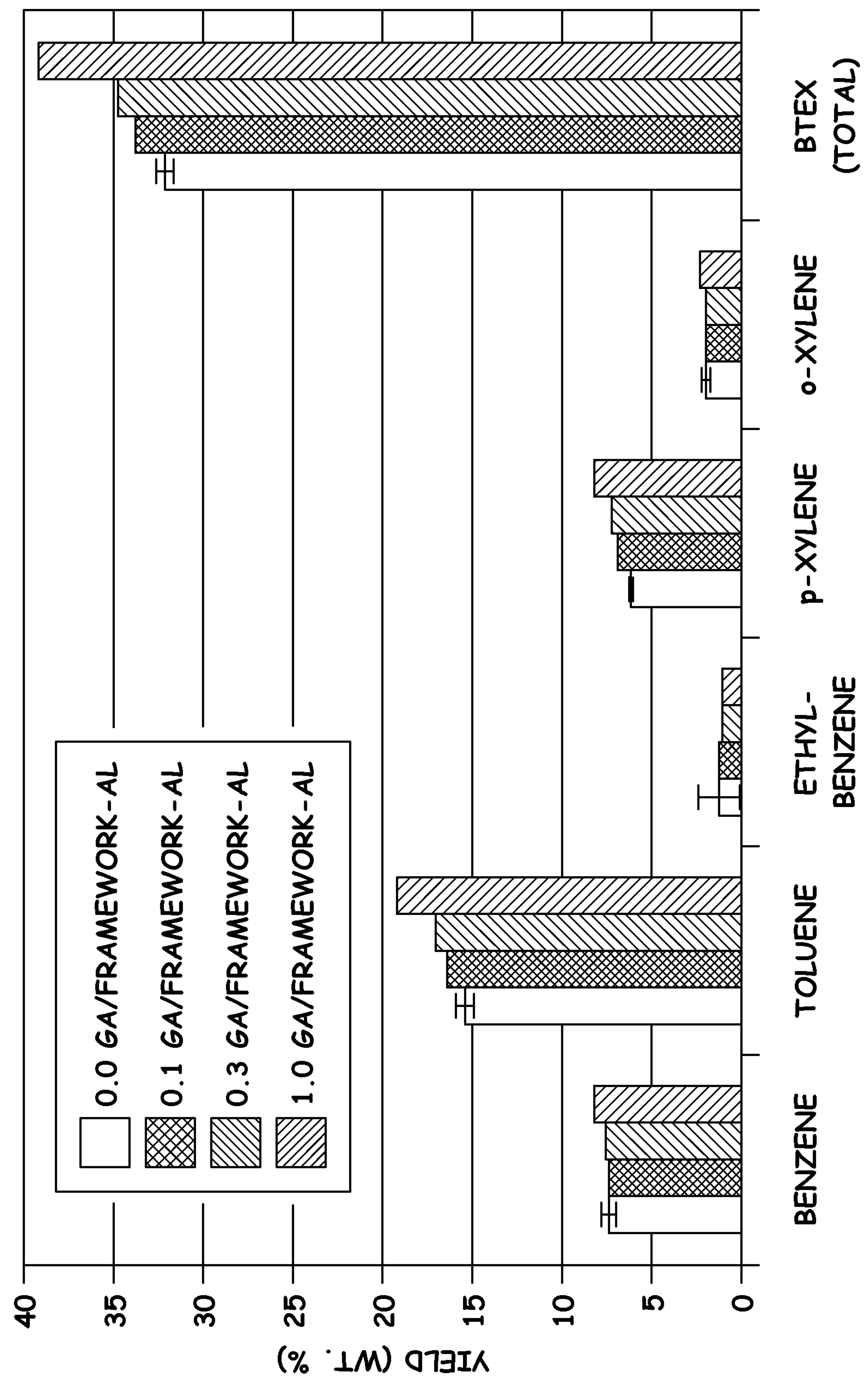

Fig. 6

(CANOLA OIL)

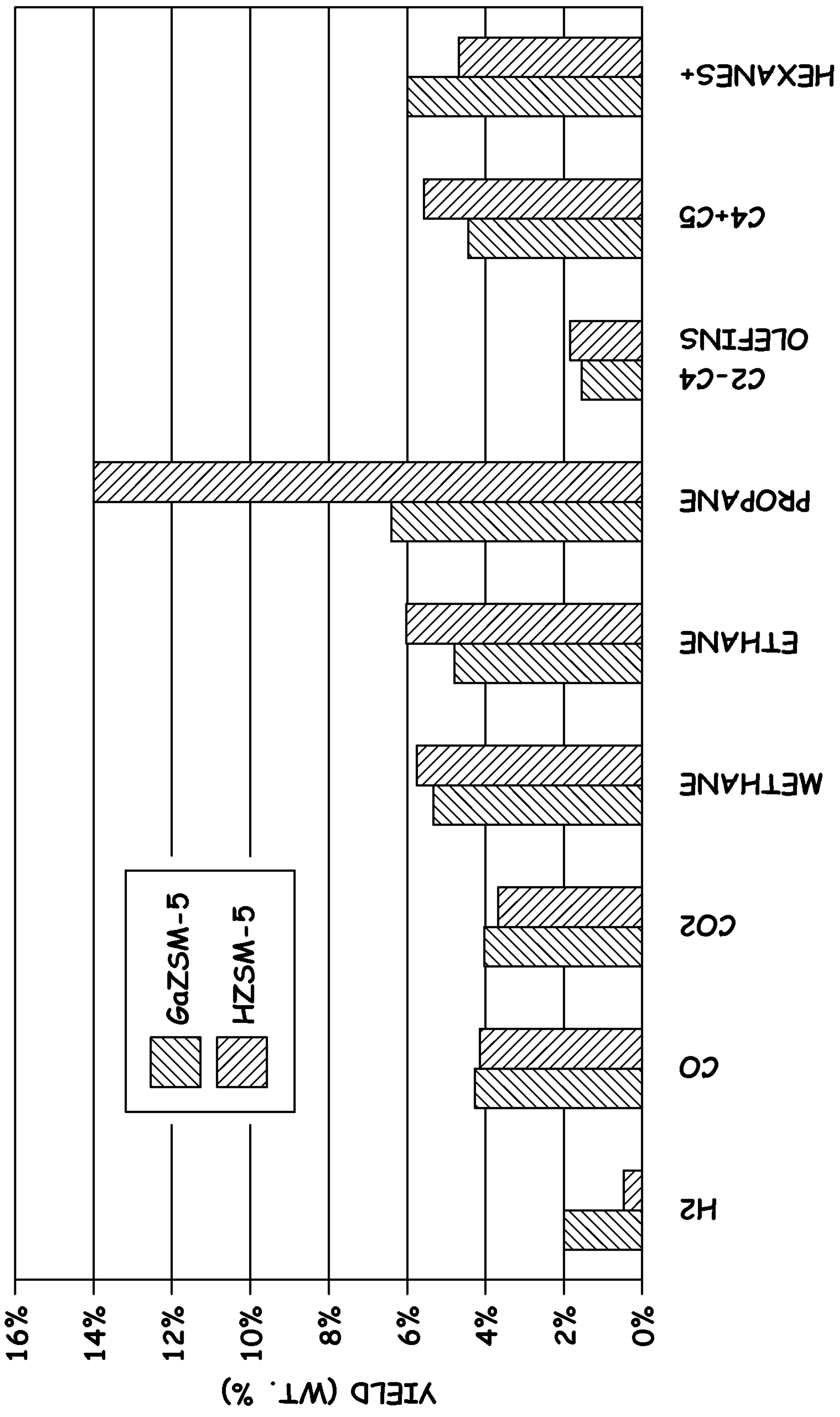

Fig. 7
(ALGAE OIL)

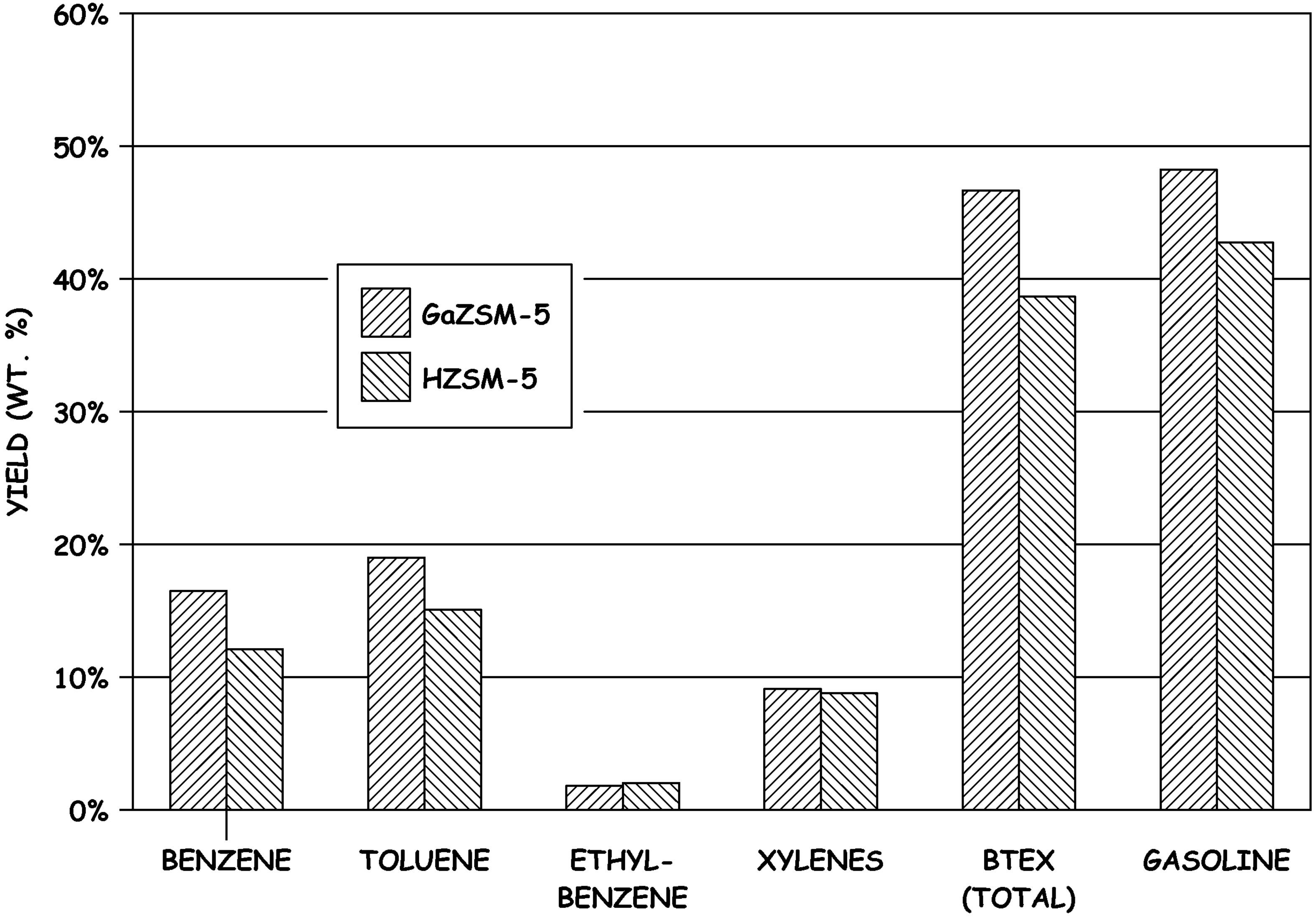

Fig. 8

(ALGAE OIL)

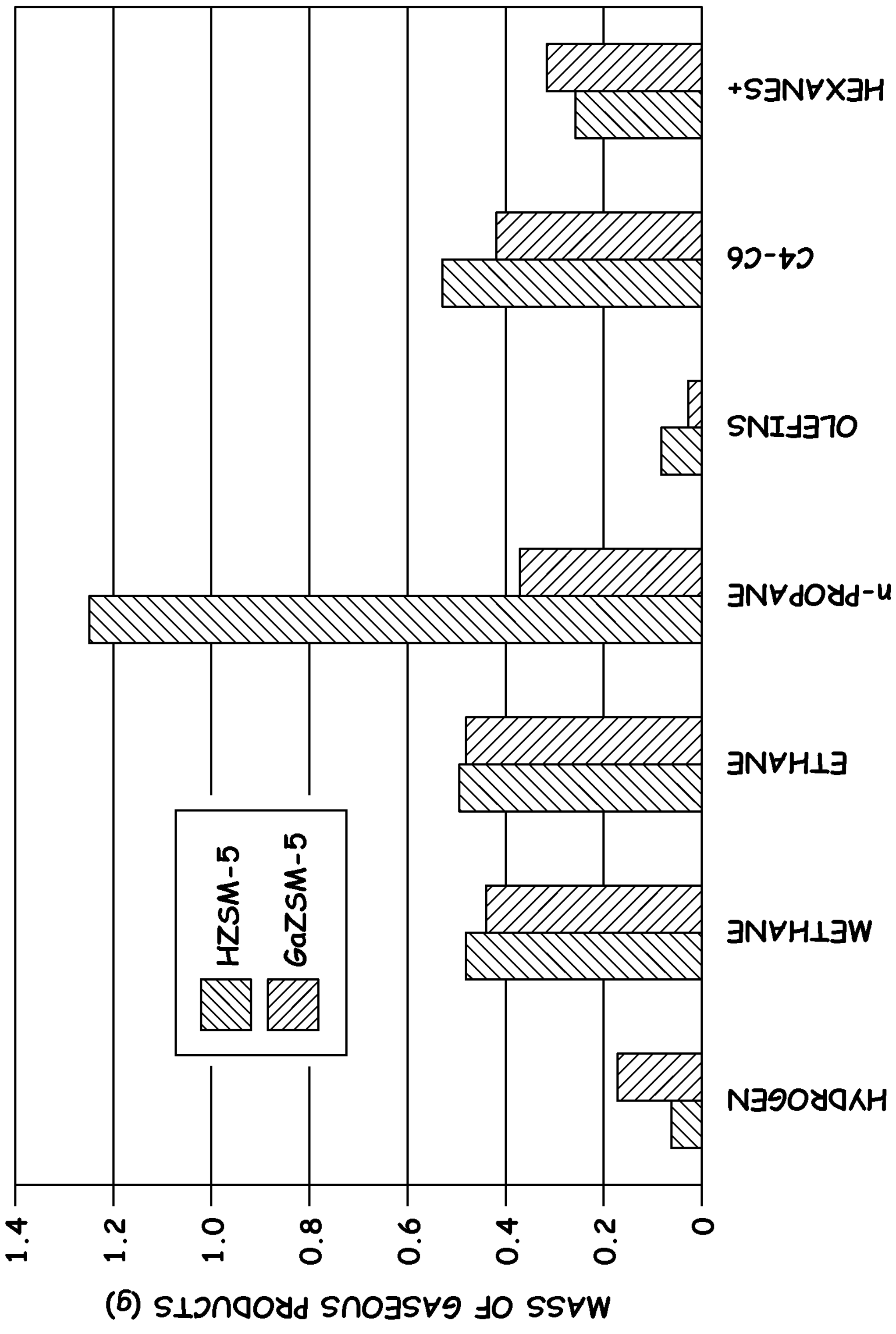
MASS OF GASEOUS PRODUCTS (g)
1.4
1.2
1.0
0.8
0.6
0.4
0.2
0
HZSM-5
GaZSM-5
HYDROGEN
METHANE
ETHANE
n-PROPANE
OLEFINS
C4-C6
HEXANES+

Fig. 9
(GAS OIL)

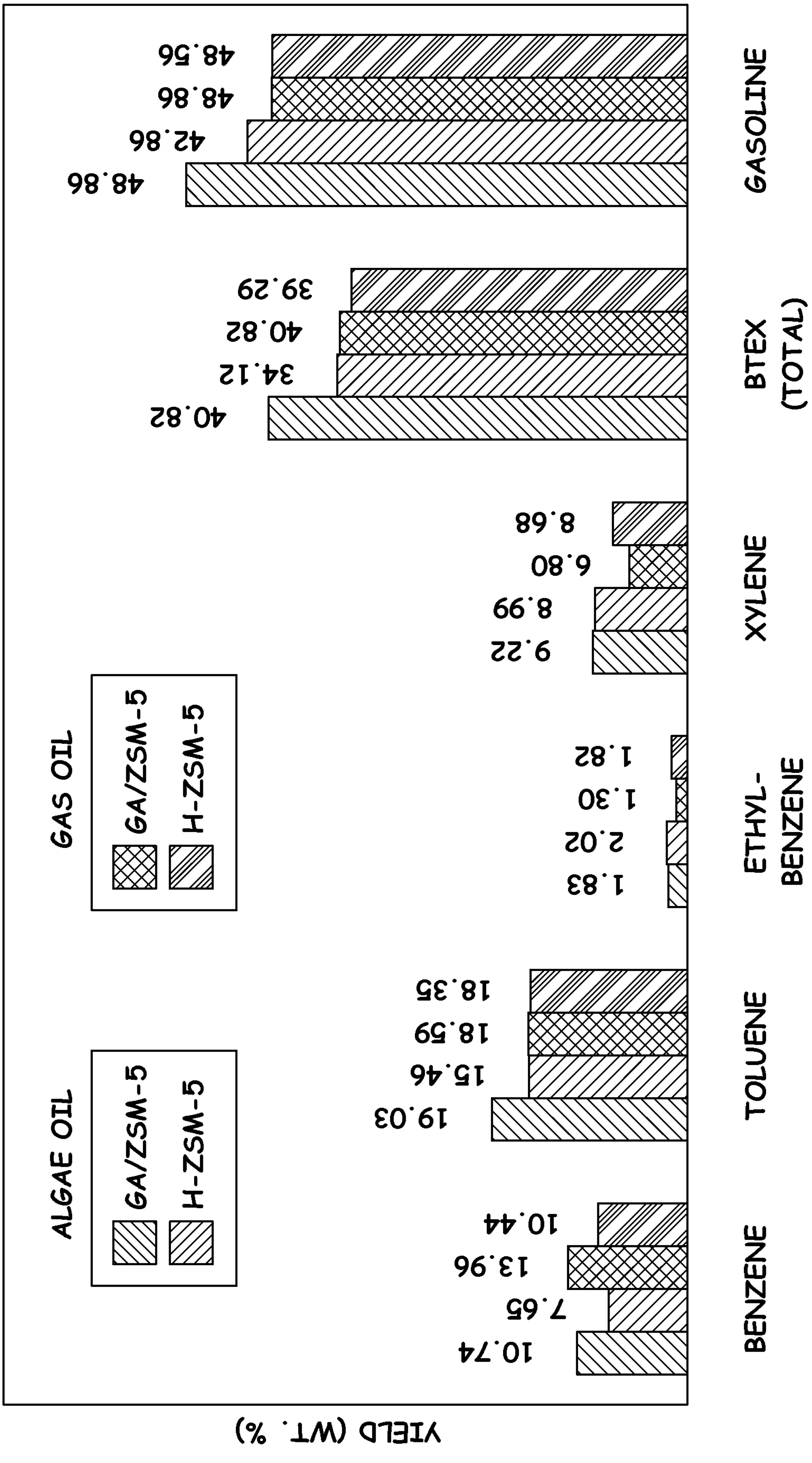
YIELD (WT. %)
ALGAE OIL
GA/ZSM-5
H-ZSM-5
GAS OIL
GA/ZSM-5
H-ZSM-5
BENZENE
10.74
7.65
13.96
10.44
TOLUENE
19.03
15.46
18.59
18.35
ETHYL-BENZENE
1.83
2.02
1.30
1.82
XYLENE
9.22
8.99
6.80
8.68
BTEX (TOTAL)
40.82
34.12
40.82
39.29
GASOLINE
48.86
42.86
48.86
48.56

Fig. 10

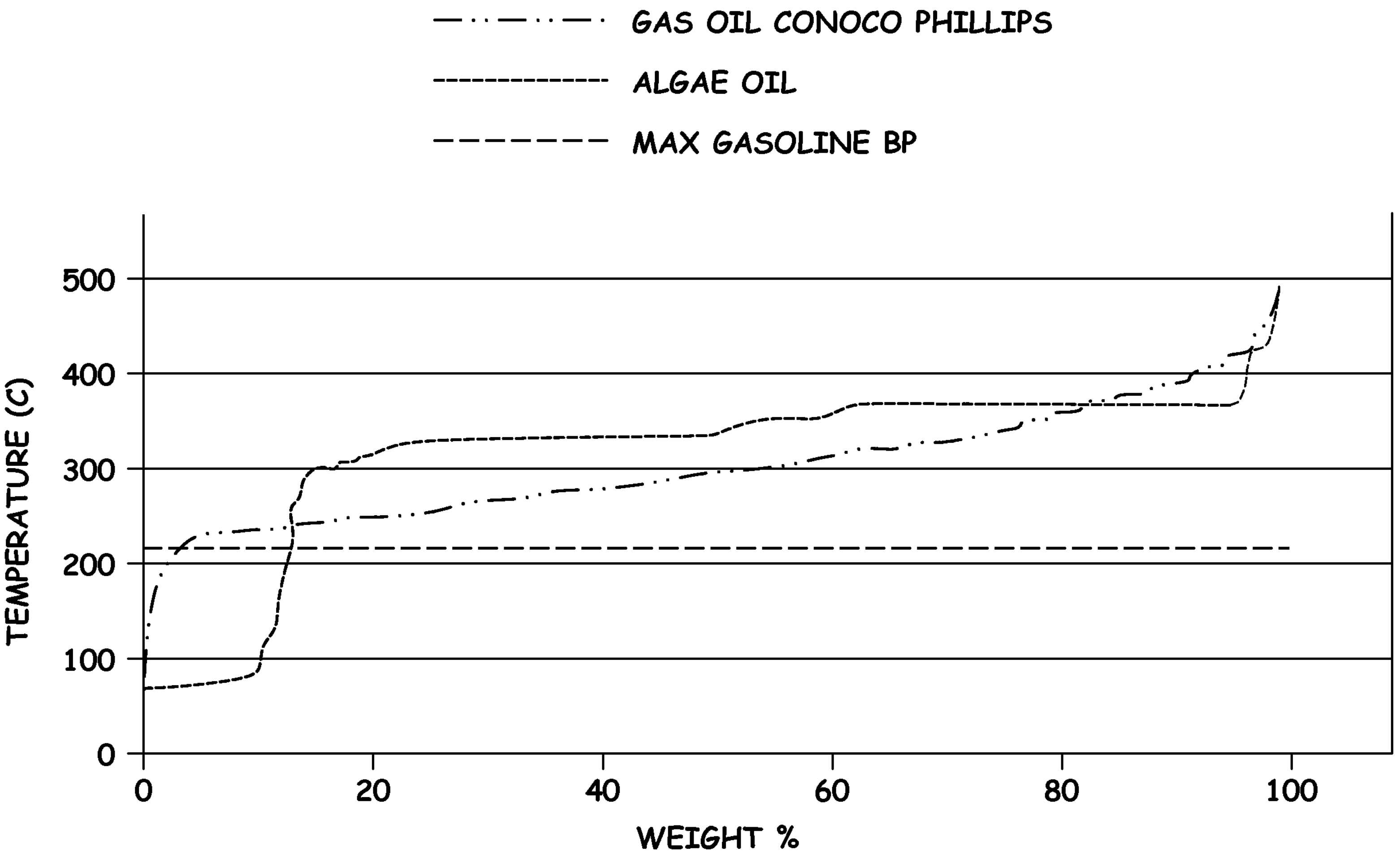
GAS OIL CONOCO PHILLIPS
ALGAE OIL
MAX GASOLINE BP
TEMPERATURE (C)
500
400
300
200
100
0
0
20
40
60
80
100
WEIGHT %

Fig. 11

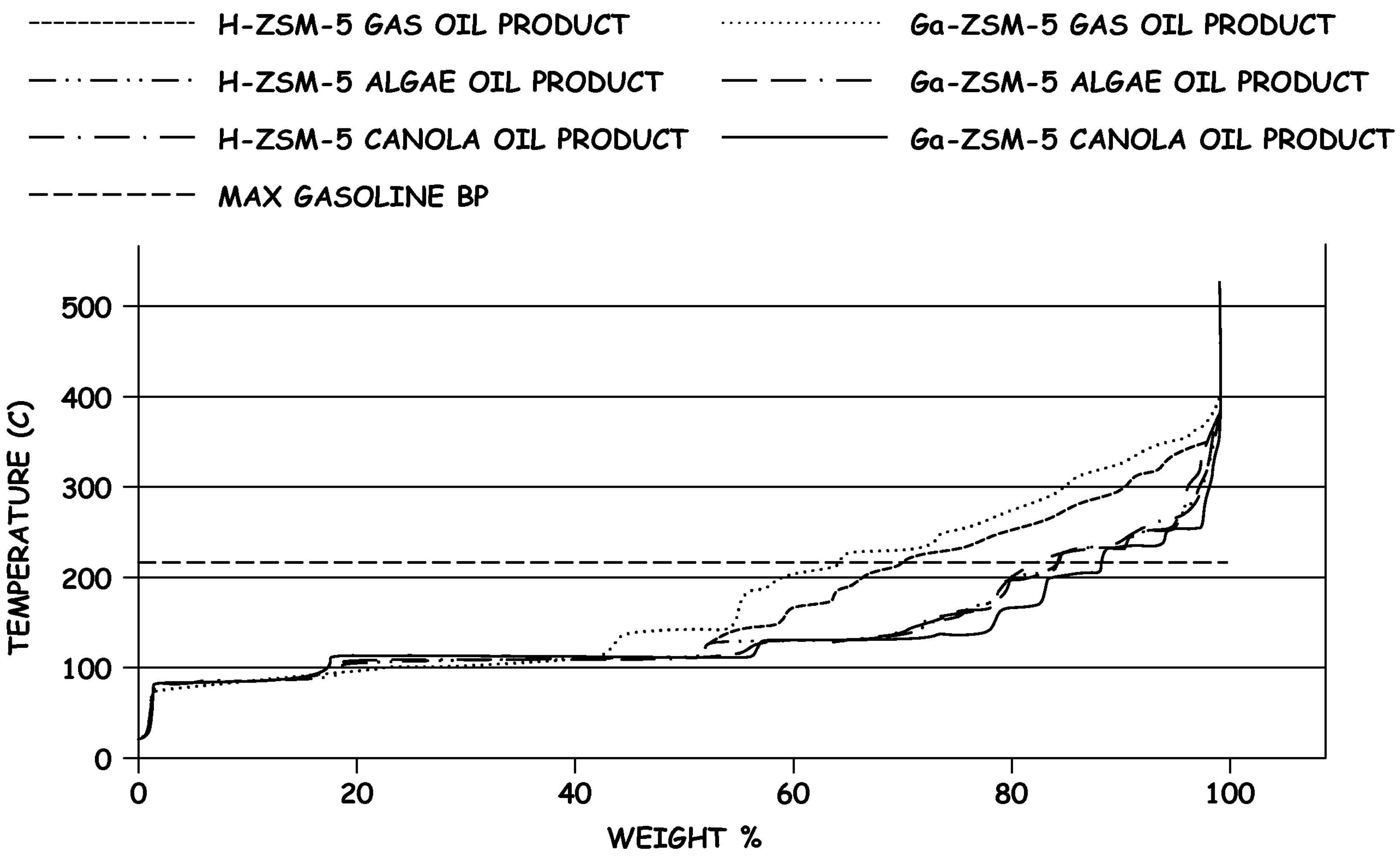
H-ZSM-5 GAS OIL PRODUCT
H-ZSM-5 ALGAE OIL PRODUCT
H-ZSM-5 CANOLA OIL PRODUCT
MAX GASOLINE BP
Ga-ZSM-5 GAS OIL PRODUCT
Ga-ZSM-5 ALGAE OIL PRODUCT
Ga-ZSM-5 CANOLA OIL PRODUCT
TEMPERATURE (C)
500
400
300
200
100
0
0
20
40
60
80
100
WEIGHT %

Fig. 12

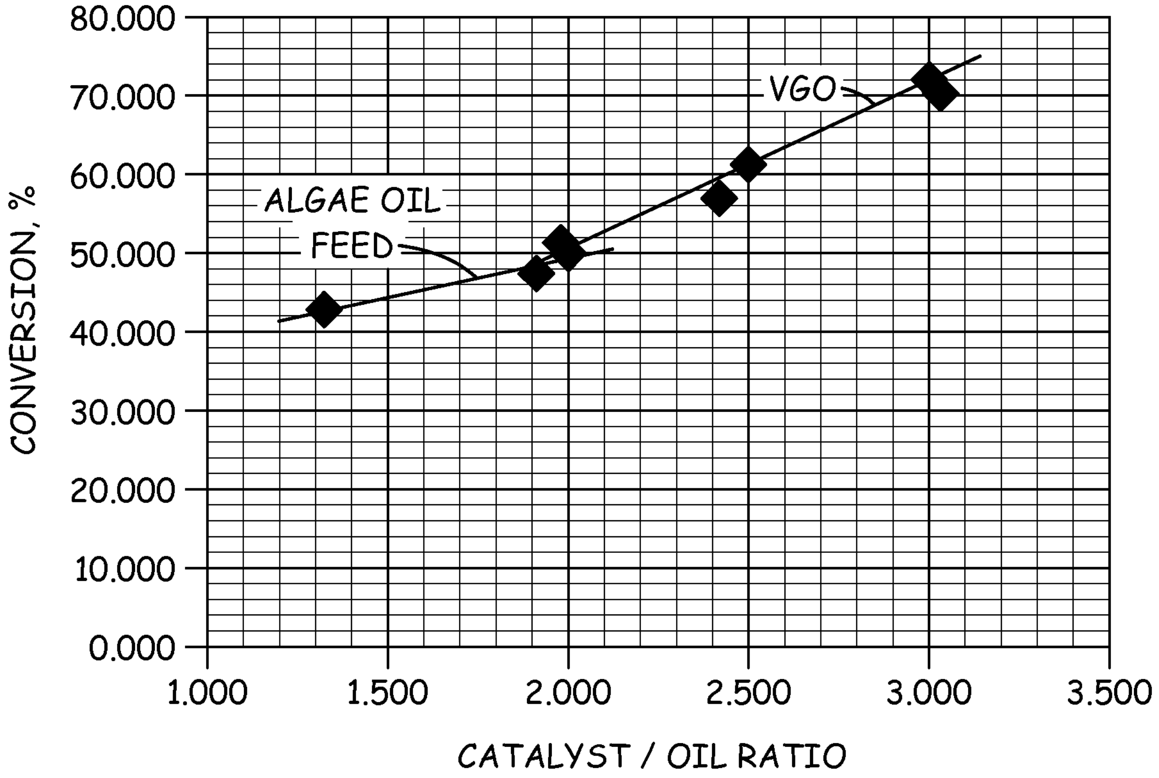
80.000
70.000
60.000
50.000
40.000
30.000
20.000
10.000
0.000
CONVERSION, %
1.000
1.500
2.000
2.500
3.000
3.500
CATALYST / OIL RATIO
ALGAE OIL FEED
VGO

Fig. 13

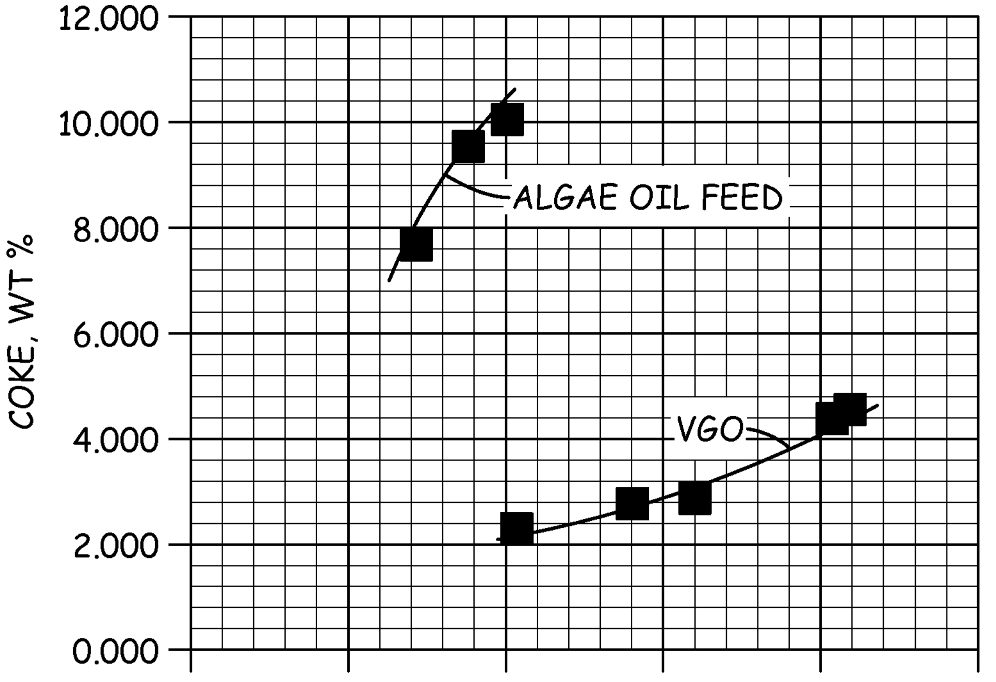
12.000
10.000
8.000
6.000
4.000
2.000
0.000
COKE, WT %
30.000
40.000
50.000
60.000
70.000
80.000
CONVERSION, %
ALGAE OIL FEED
VGO

Fig. 14

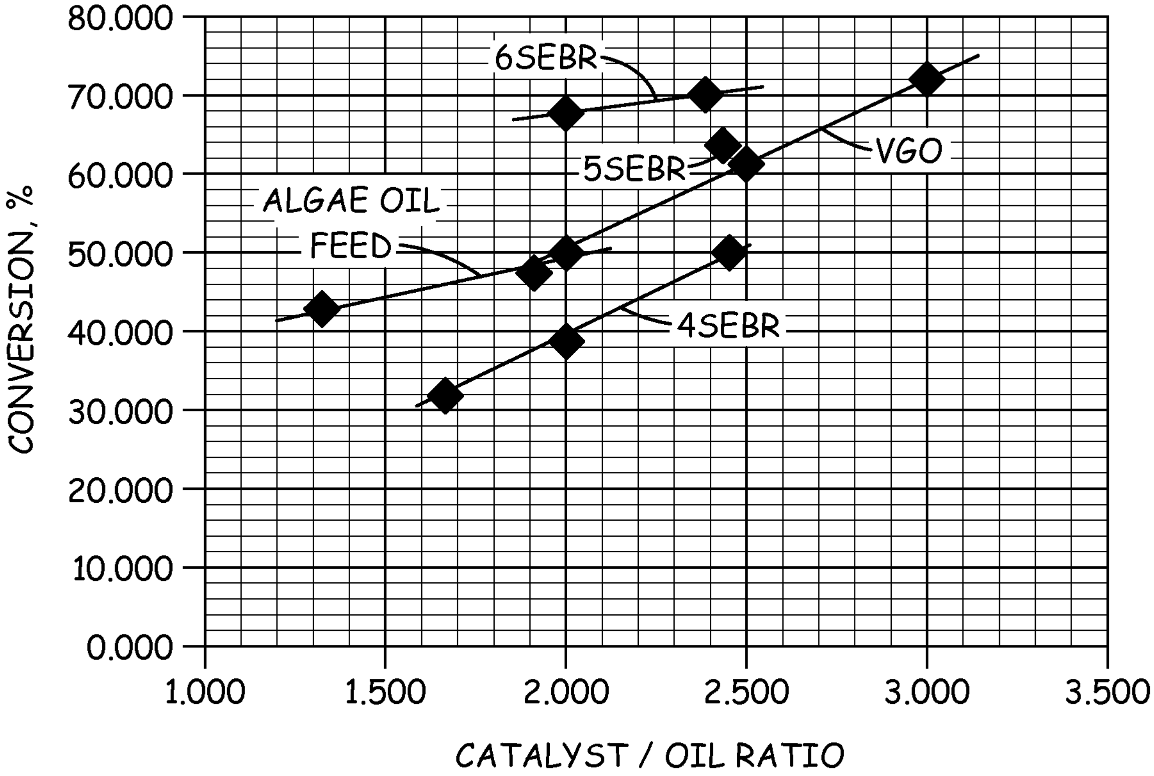
80.000
70.000
60.000
50.000
40.000
30.000
20.000
10.000
0.000
CONVERSION, %
1.000
1.500
2.000
2.500
3.000
3.500
CATALYST / OIL RATIO
6SEBR
5SEBR
VGO
ALGAE OIL FEED
4SEBR

Fig. 15

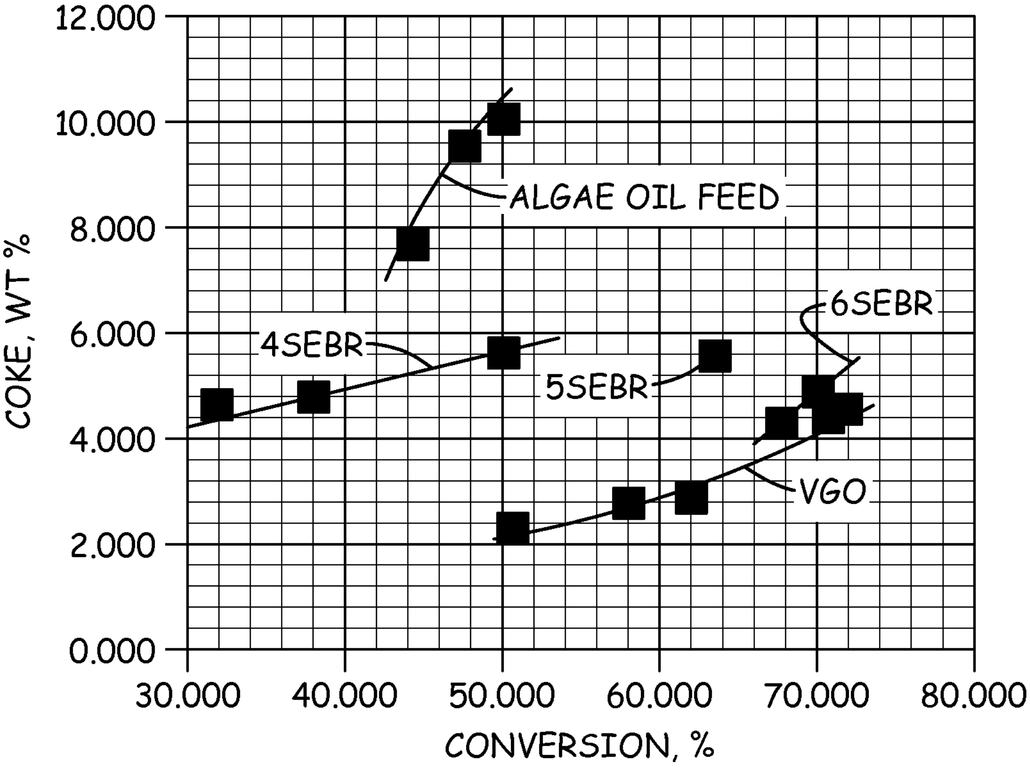
12.000
10.000
8.000
6.000
4.000
2.000
0.000
COKE, WT %
30.000
40.000
50.000
60.000
70.000
80.000
CONVERSION, %
ALGAE OIL FEED
4SEBR
5SEBR
6SEBR
VGO

Fig. 16

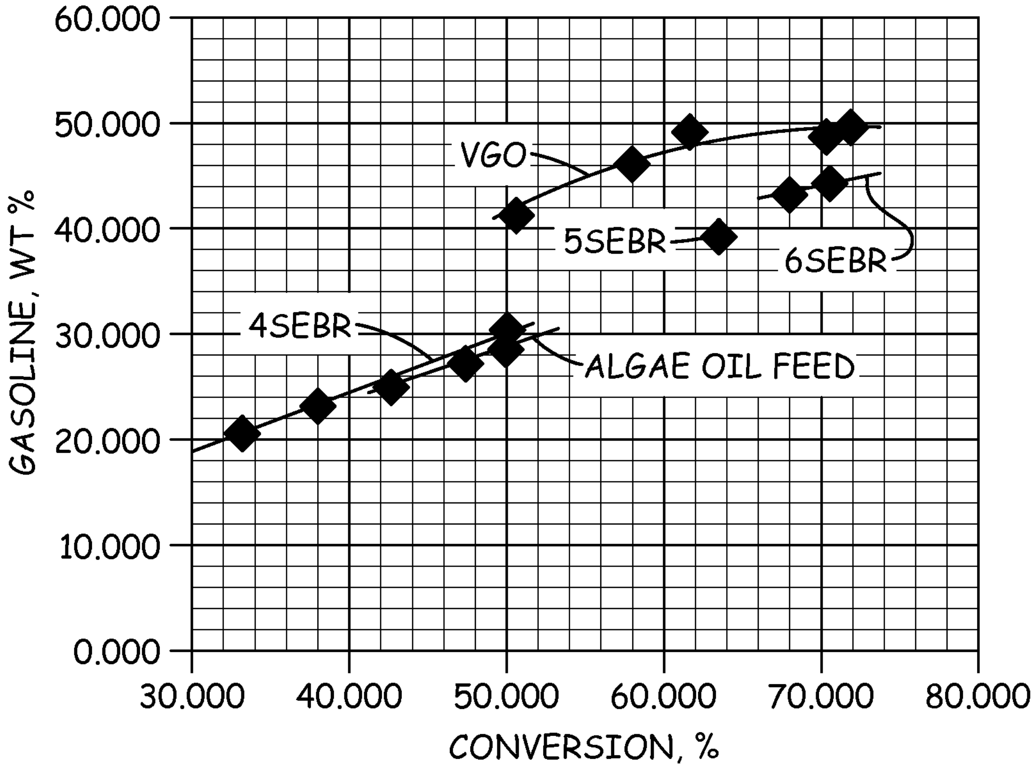
60.000
50.000
40.000
30.000
20.000
10.000
0.000
GASOLINE, WT %
30.000
40.000
50.000
60.000
70.000
80.000
CONVERSION, %
VGO
5SEBR
6SEBR
4SEBR
ALGAE OIL FEED

Fig. 17

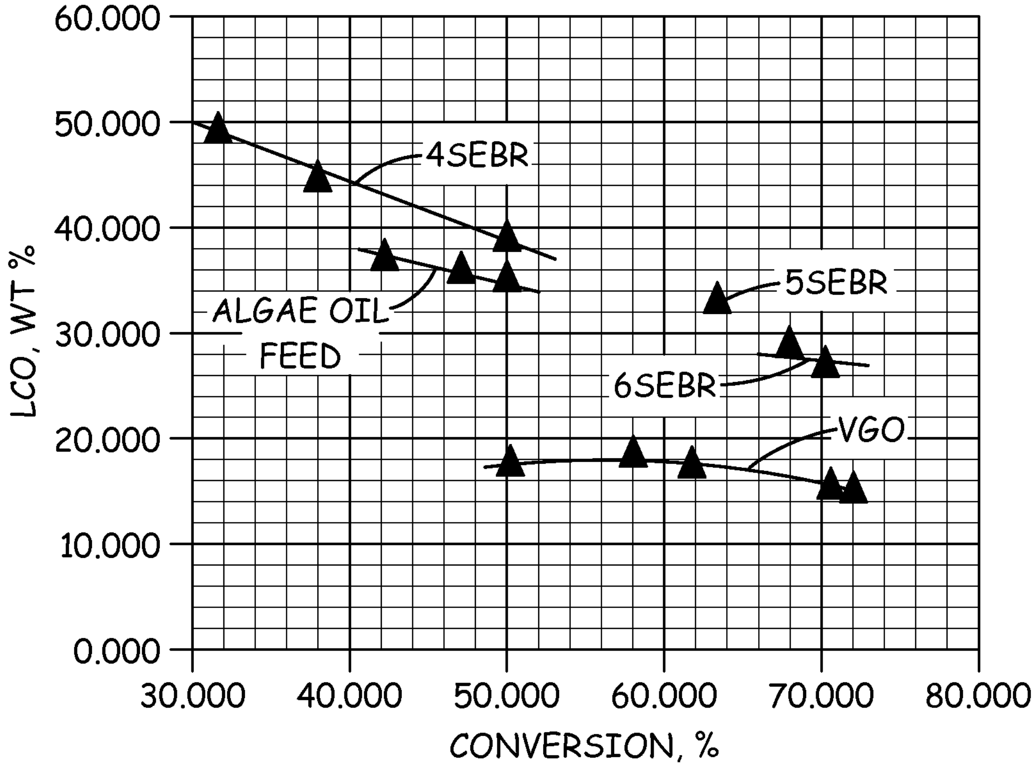
60.000
50.000
40.000
30.000
20.000
10.000
0.000
LCO, WT %
30.000
40.000
50.000
60.000
70.000
80.000
CONVERSION, %
4SEBR
ALGAE OIL FEED
5SEBR
6SEBR
VGO

Fig. 18

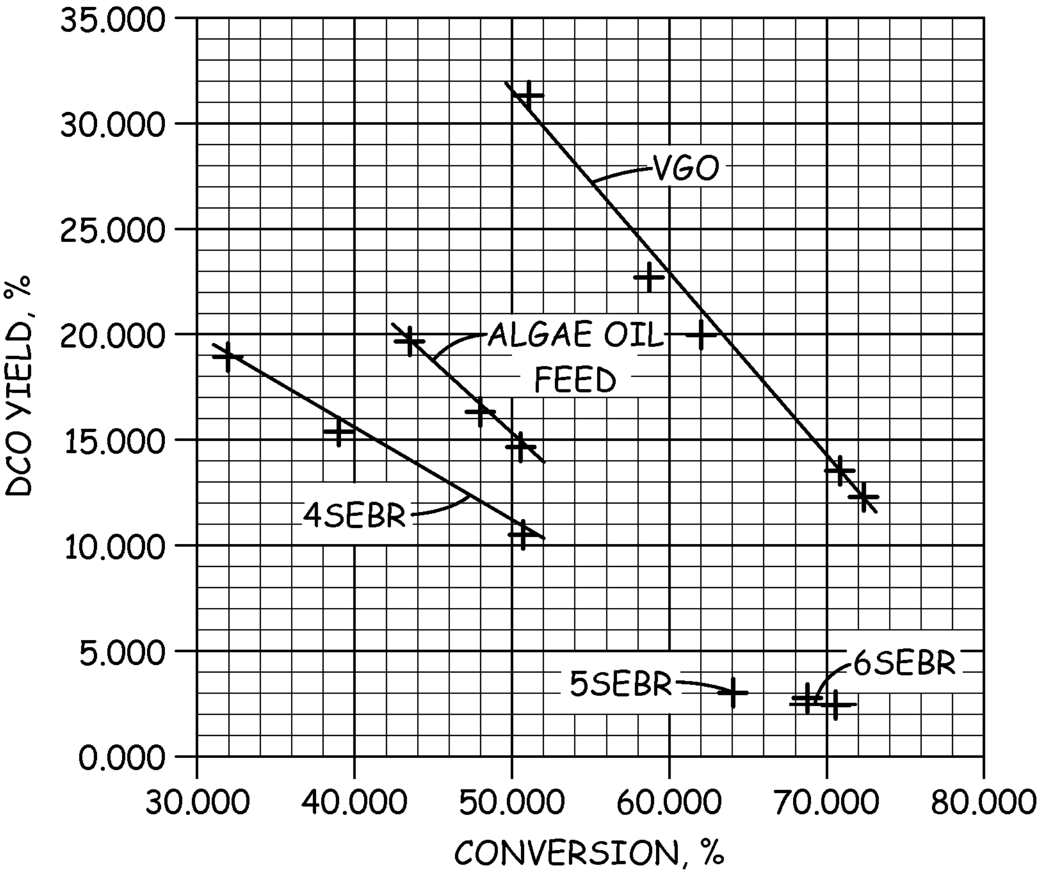
35.000
30.000
25.000
20.000
15.000
10.000
5.000
0.000
DCO YIELD, %
30.000
40.000
50.000
60.000
70.000
80.000
CONVERSION, %
VGO
ALGAE OIL FEED
4SEBR
5SEBR
6SEBR

Fig. 19

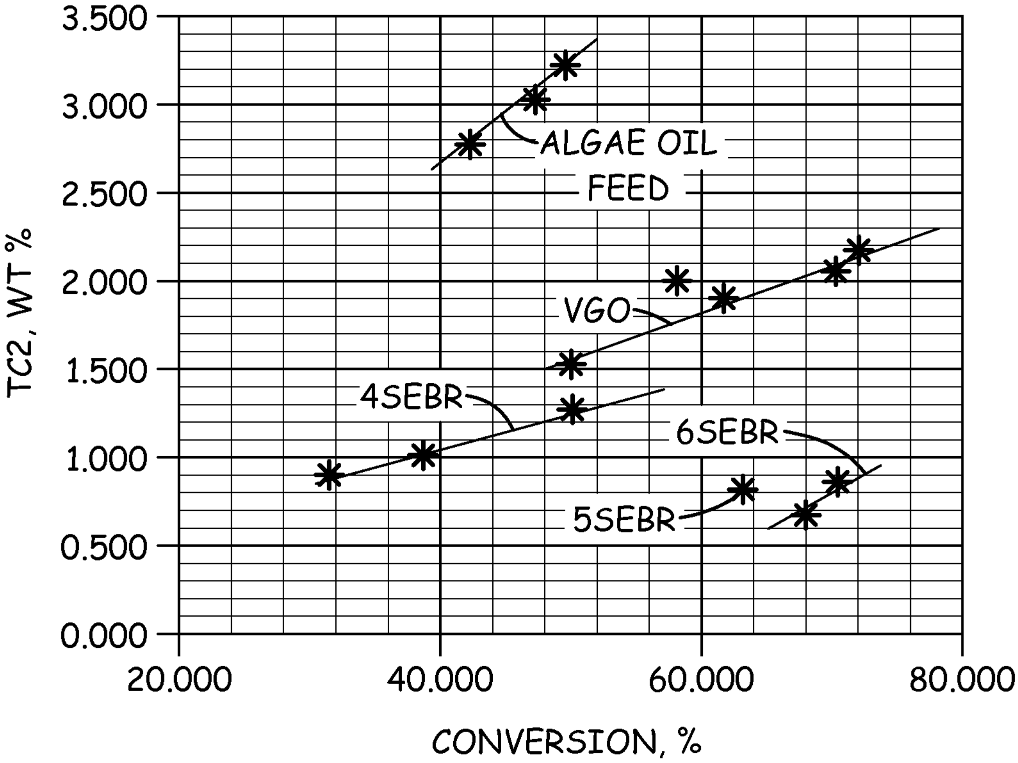
3.500
3.000
2.500
2.000
1.500
1.000
0.500
0.000
TC2, WT %
20.000
40.000
60.000
80.000
CONVERSION, %
ALGAE OIL FEED
VGO
4SEBR
6SEBR
5SEBR

Fig. 20

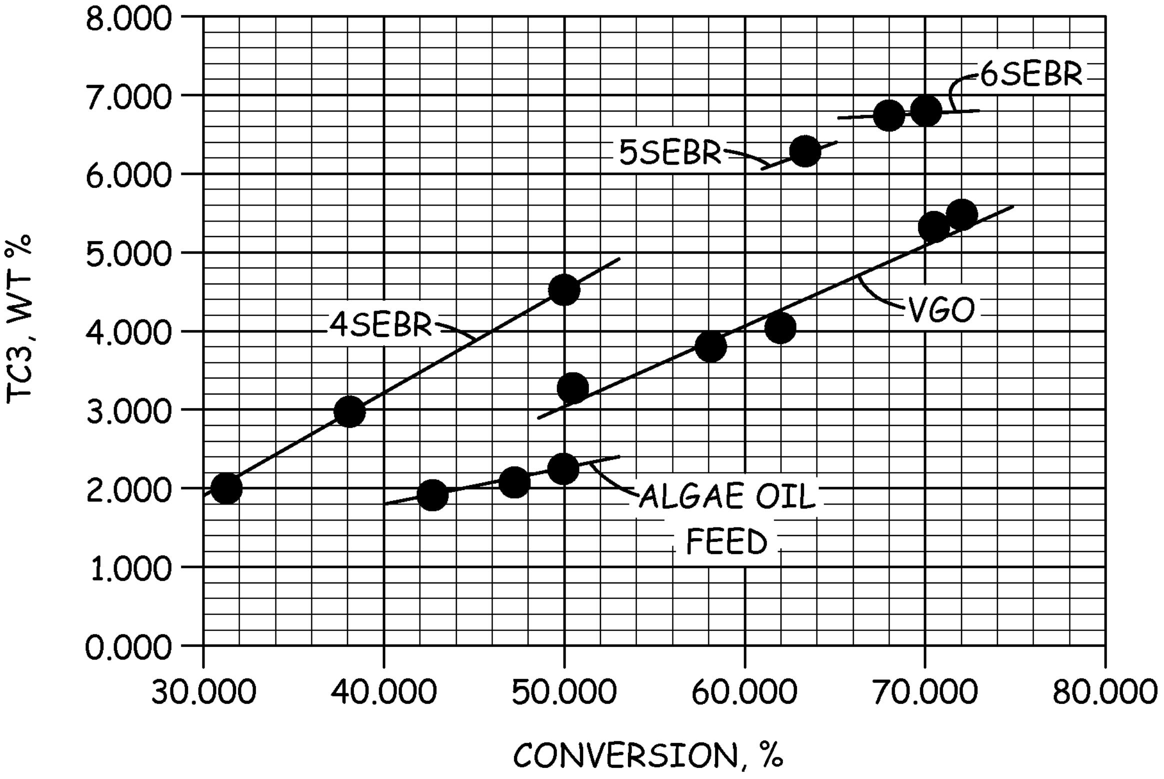
8.000
7.000
6.000
5.000
4.000
3.000
2.000
1.000
0.000
TC3, WT %
30.000
40.000
50.000
60.000
70.000
80.000
CONVERSION, %
6SEBR
5SEBR
4SEBR
VGO
ALGAE OIL FEED

Fig. 21

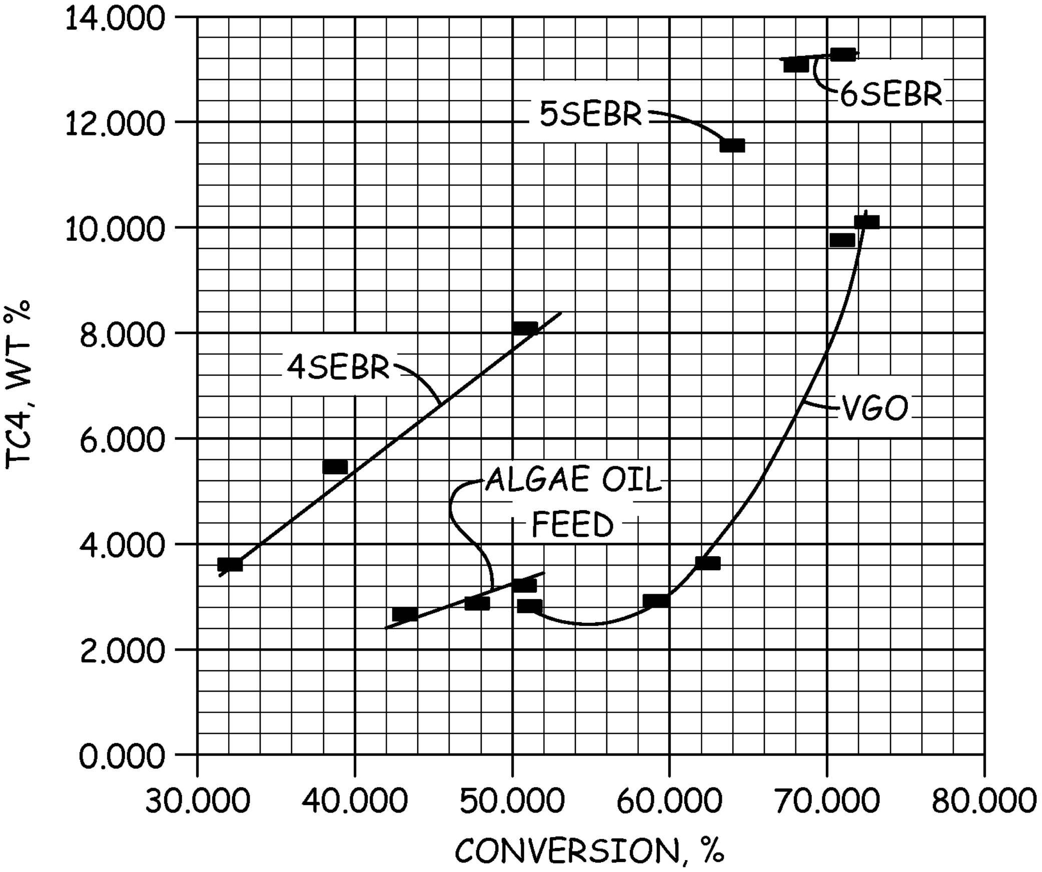
14.000
12.000
10.000
8.000
6.000
4.000
2.000
0.000
TC4, WT %
30.000
40.000
50.000
60.000
70.000
80.000
CONVERSION, %
6SEBR
5SEBR
4SEBR
VGO
ALGAE OIL FEED

Fig. 22

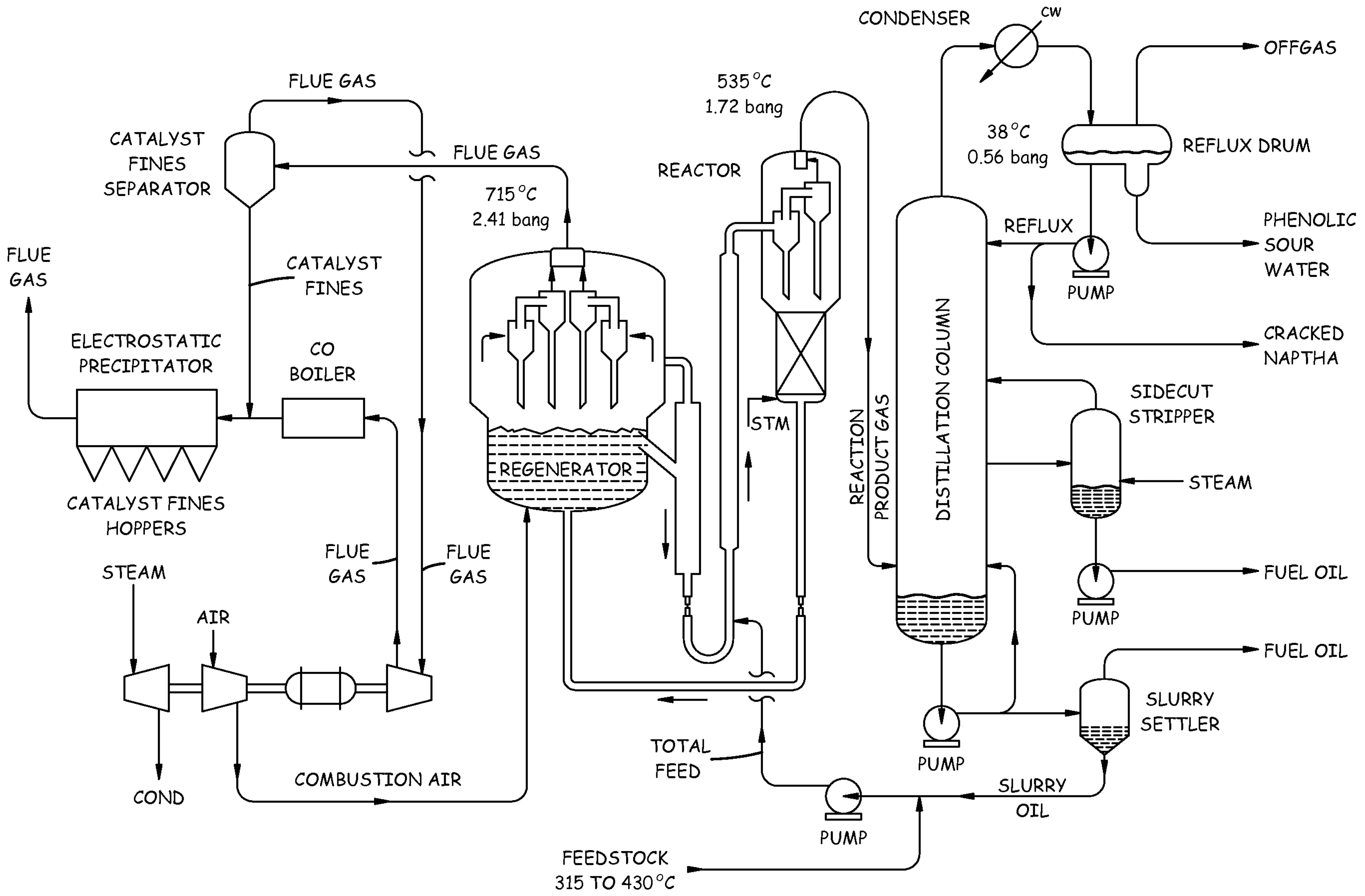
FLUE GAS
CATALYST FINES SEPARATOR
FLUE GAS
715 °C
2.41 bang
535 °C
1.72 bang
REACTOR
CONDENSER
CW
38 °C
0.56 bang
REFLUX DRUM
OFFGAS
PHENOLIC SOUR WATER
REFLUX
PUMP
CRACKED NAPTHA
FLUE GAS
CATALYST FINES
ELECTROSTATIC PRECIPITATOR
CO BOILER
REGENERATOR
STM
REACTION PRODUCT GAS
DISTILLATION COLUMN
SIDECUT STRIPPER
STEAM
CATALYST FINES HOPPERS
FLUE GAS
FLUE GAS
FUEL OIL
PUMP
STEAM
AIR
FUEL OIL
SLURRY SETTLER
TOTAL FEED
PUMP
COND
COMBUSTION AIR
SLURRY OIL
PUMP
FEEDSTOCK
315 TO 430 °C

Fig. 23

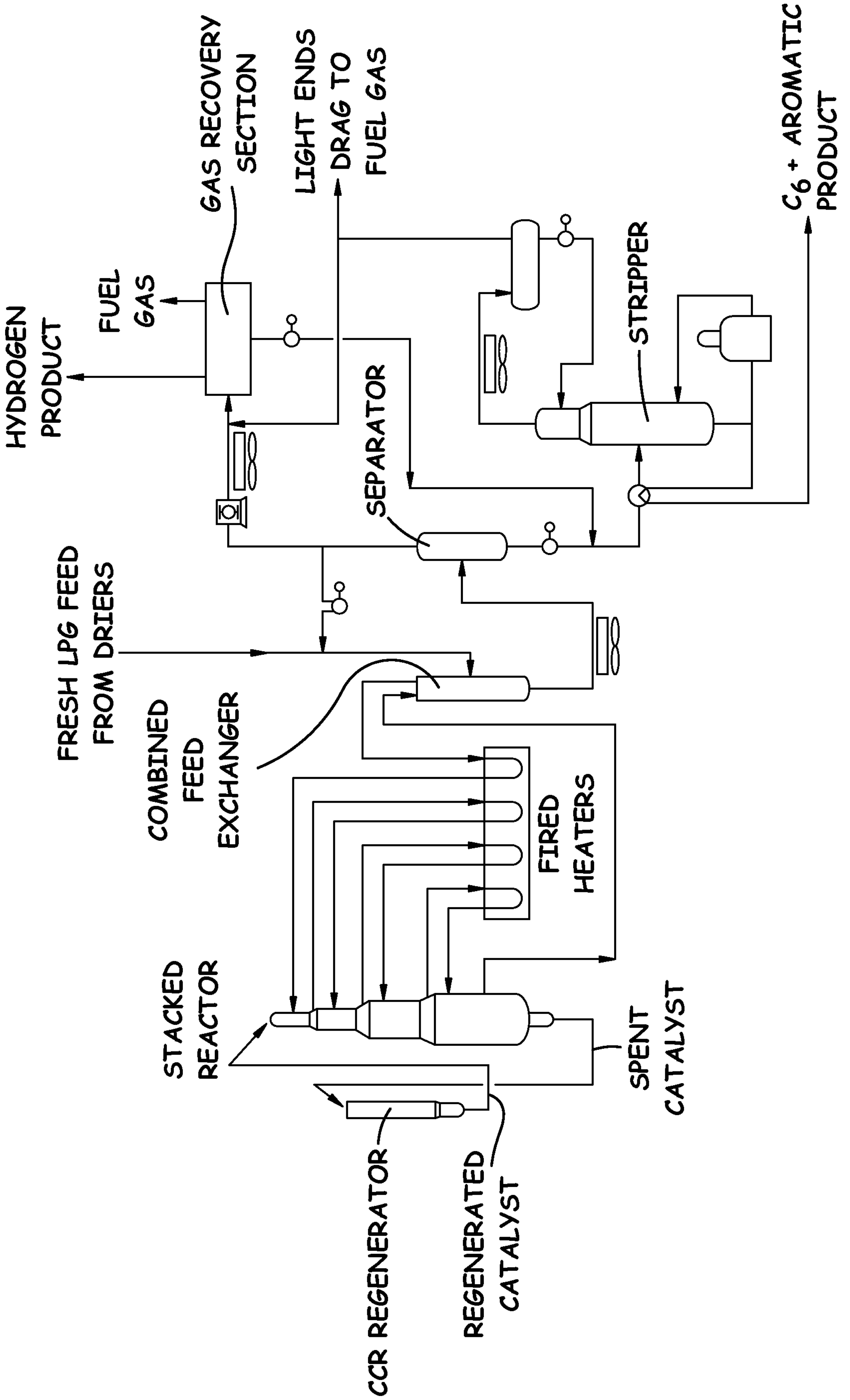
HYDROGEN PRODUCT
FUEL GAS
GAS RECOVERY SECTION
LIGHT ENDS DRAG TO FUEL GAS
C_6 + AROMATIC PRODUCT
STRIPPER
SEPARATOR
FRESH LPG FEED FROM DRIERS
COMBINED FEED EXCHANGER
FIRED HEATERS
STACKED REACTOR
SPENT CATALYST
CCR REGENERATOR
REGENERATED CATALYST

Fig. 24

INTERNATIONAL SEARCH REPORT	International application No. **PCT/US2011/067444**

A. CLASSIFICATION OF SUBJECT MATTER Int. Cl. *C10G 3/00* (2006.01) *C10G 45/60* (2006.01) *B01J 23/08* (2006.01) *C10G 45/64* (2006.01) *C07C 1/213* (2006.01) According to International Patent Classification (IPC) or to both national classification and IPC	
B. FIELDS SEARCHED	
Minimum documentation searched (classification system followed by classification symbols)	
Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched	
Electronic data base consulted during the international search (name of data base and, where practicable, search terms used) WPI, EPODOC with class marks; C10G , C07C , C01L , B01J19, B01J8 , B01J23/08 and Keywords; biomass, renewable, algae, vegetable, seed, nut, corn, sun flower, sorghum, soy, canola , palm, fungi, bacteria , bio oil, oil, lipid, fat, glyceride, "BTEX","BTX", benzene, "C6H6", toluene, C7H8, xylene, ethyl benzene, "C8H10", aromatic, diesel, gasoline, cracking, reform, catalyst, gallium, "Ga" and like terms . Full Text databases: ESPACENET and USPTO with above keywords.	

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
	US 2009/0318740 A1 (GUILLON et al.) 24 December 2009	
X	Abstract, Example 1 and paragraphs [0029], [0036], [0062], [0072] & [0114]	1, 3 - 8, 10 -12, 18, 20 - 22, 26 - 32, 37 - 51, 54
Y	As above	13 – 17, 23 - 25, 34-36, 47 -50
Y	As above	52, 53
	Derwent Abstract Accession No. 2011-F58298 [38]; WO 2011/062410 A2 (KOREA INSTITUTE OF ENERGY RESEARCH [KR]) 26 May 2011	
X	Abstract	1 - 3, 6 - 8, 28 -32, 40, 54
	US 2007/0007176 A1 (PINHO et al.) 11 January 2007	
Y	Abstract, claim 5 and paragraphs [0017] to [0018]	13 – 17, 23 – 25, 34 – 36, 47 -50

☒ Further documents are listed in the continuation of Box C ☒ See patent family annex

*	Special categories of cited documents:		
"A"	document defining the general state of the art which is not considered to be of particular relevance	"T"	later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"E"	earlier application or patent but published on or after the international filing date	"X"	document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"L"	document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	"Y"	document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"O"	document referring to an oral disclosure, use, exhibition or other means	"&"	document member of the same patent family
"P"	document published prior to the international filing date but later than the priority date claimed		

Date of the actual completion of the international search 19 February 2012	Date of mailing of the international search report 24 February 2012
Name and mailing address of the ISA/AU AUSTRALIAN PATENT OFFICE PO BOX 200, WODEN ACT 2606, AUSTRALIA E-mail address: pct@ipaustralia.gov.au Facsimile No. +61 2 6283 7999	Authorized officer **KOSALA GUNATILLAKA** AUSTRALIAN PATENT OFFICE (ISO 9001 Quality Certified Service) Telephone No : +61 2 6222 3652

INTERNATIONAL SEARCH REPORT	International application No. PCT/US2011/067444

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US 2009/0126260 A1 (ARAVANIS et al.) 21 May 2009 Paragraphs [0011] and [0099]	52, 53
P, X	WO 2011/126817 A2 (UOP LLC [US]) 13 October 2011 Abstract, paragraphs [0004], [0011] – [0012] and claims 1,2, 6 & 12	1, 4, 10, 15, 16, 28, 40, 43 - 45, 51
A	WO 2007/062825 A1 (ASER S R L [IT]) 07 June 2007 Abstract, examples and Claims 1 - 6	1 – 39, 54
A	WO 2010/068255 A1 (W.R. GRACE & CO. - CONN. [US]) 17 June 2010 Abstract and paragraphs [0010] – [0016] and claims 1 – 6	1 – 54

This Annex lists the known "A" publication level patent family members relating to the patent documents cited in the above-mentioned international search report. The Australian Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

Patent Document Cited in Search Report		Patent Family Member					
US	2009318740	BR	PI0903654	EP	2138552	FR	2932811
		JP	2010047744	SG	158051		
WO	2011062410	KR	20110054298				
US	2007007176	AR	055799	BR	PI0502577	US	7540952
US	2009126260	AR	071247	AU	2008302339	CA	2698908
		CN	101855320	EP	2205697	GB	2454853
		JP	2010539300	KR	20100084628	MX	2010002821
		US	8075641	WO	2009039015	WO	2009039201
WO	2007062825	IT	MI20052303				
WO	2010068255	AR	074567	AU	2009325130	CA	2746167
		CN	102245170	CO	6341544	EP	2373291
		KR	20110097931	MX	2011005585	SG	171982
		TW	201028464	US	2011224471		

Due to data integration issues this family listing may not include 10 digit Australian applications filed since May 2001.

END OF ANNEX