



(51) International Patent Classification:

C07C 1/00 (2006.01) C07C 1/24 (2006.01)
C07C 1/02 (2006.01) C07C 1/213 (2006.01)
C07C 1/20 (2006.01)

(21) International Application Number:

PCT/US2015/034621

(22) International Filing Date:

8 June 2015 (08.06.2015)

(25) Filing Language:

English

(26) Publication Language:

English

(30) Priority Data:

62/009,605 9 June 2014 (09.06.2014) US

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(81) Designated States (unless otherwise indicated, for every kind of national protection available): AE, AG, AL, AM, AO, AT, AU, AZ, BA, BB, BG, BH, BN, BR, BW, BY, BZ, CA, CH, CL, CN, CO, CR, CU, CZ, DE, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IR, IS, JP, KE, KG, KN, KP, KR, KZ, LA, LC, LK, LR, LS, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PA, PE, PG, PH, PL, PT, QA, RO, RS, RU, RW, SA, SC, SD, SE, SG, SK, SL, SM, ST, SV, SY, TH, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.

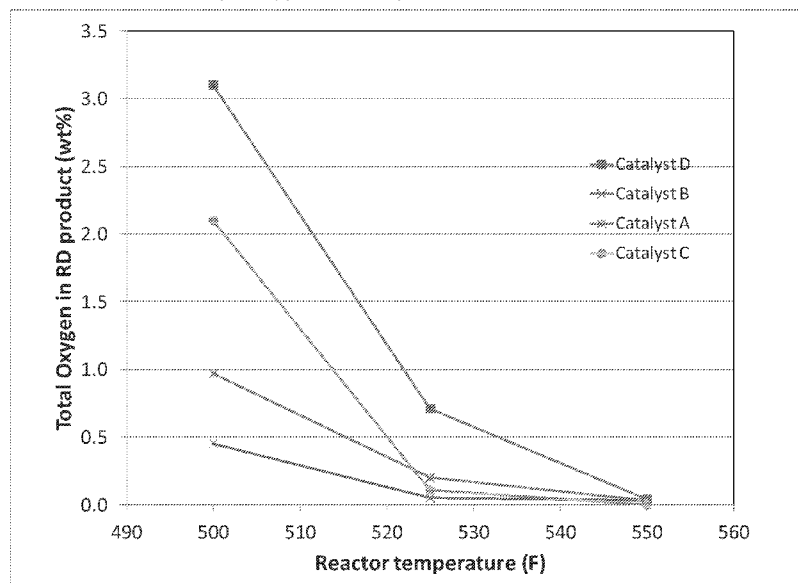
(84) Designated States (unless otherwise indicated, for every kind of regional protection available): ARIPO (BW, GH, GM, KE, LR, LS, MW, MZ, NA, RW, SD, SL, ST, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, RU, TJ, TM), European (AL, AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV, MC, MK, MT, NL, NO, PL, PT, RO, RS, SE, SI, SK, SM, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, KM, ML, MR, NE, SN, TD, TG).

Published:

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

(54) Title: METHOD FOR CATALYTIC DEOXYGENATION OF NATURAL OILS AND GREASES

Fig. 1. Oxygen conversion performance of catalysts A-D.



(57) Abstract: A method for deoxygenating renewable oils comprised of natural oils or greases or derivatives thereof containing triglycerides or free fatty acids includes the steps of: providing a catalyst comprising a support predominantly comprised of alumina with metal compounds provided on the support based on Mo and at least one selected from the group consisting of Ni and Co, and at least one selected from the group consisting of Cu and Cr, and contacting the renewable oils with the catalyst under conditions sufficient to deoxygenate the renewable oils.

**METHOD FOR CATALYTIC DEOXYGENATION OF NATURAL OILS AND
GREASES**

CROSS REFERENCE TO RELATED APPLICATION

[0001] This application claims the benefit of the filing date of United States Provisional Patent Application No. 62/009605 filed June 9, 2014, which is hereby incorporated by reference.

FIELD OF THE INVENTION

[0002] This invention relates to hydrotreating catalyst formulations and their use in a fixed bed continuous process to provide remarkably superior oxygen removal performance.

BACKGROUND

[0003] Renewable diesel can be made from natural oils and greases (vegetable oils and animal fats) in a two-step process: Step (1) deoxygenation via hydrotreating to form n-paraffins with the removal of oxygen as H₂O and/or CO/CO₂ and Step (2) isomerization/cracking of the n-paraffins formed in Step 1 to produce branched diesel and jet fuel products per need.

[0004] Currently, the deoxygenation Step (1) mentioned above is carried out commercially using a single or multi-layer catalytic bed approach and using standard hydrotreating type catalysts similar to those used for petroleum desulfurization and

1 denitrogenation applications. The catalysts are typically based on Ni, Mo and
2 optionally P on an extruded support containing predominantly Al_2O_3 . The catalysts
3 are prepared as oxides during the manufacturing process and subsequently converted
4 to the active sulfided state either with *in situ* or *ex situ* activation procedures.

5 **[0005]** Examples of other active sites that may be employed to provide the
6 deoxygenation and hydrogenation functions are sulfided base metals such as sulfided
7 NiMo or sulfided CoMo or sulfided NiW. A base metal is a metal which oxidizes
8 when heated in air. In addition to nickel, molybdenum and tungsten, other base metals
9 which may be catalyst components herein include iron, lead, zinc, copper, tin,
10 germanium, chromium, titanium, cobalt, rhenium, indium, gallium, uranium,
11 dysprosium, thallium and mixtures thereof. While the reference uses a NiMo catalyst,
12 this reference does not specifically teach or exemplify Cu or Cr as a promoter.

13 **[0006]** US Patent Application No. 20110258916 teaches a hydrotreating
14 process that is performed in presence of hydrogen and of a hydrogenation catalyst
15 containing a support and one or more metals selected from among metals of group
16 VIII and group VIB (Group 6- chromium group.) Paragraph [0043] therein teaches
17 that the catalysts that can be used are all hydrogenation and hydrotreating catalysts
18 known in the art, and containing one or more metals selected from metals of group
19 VIII (Fe, Co, Ni, Ru, Rh, Pd, Os, Ir, Pt) and group VIB (Cr, Mo, W) suitably
20 supported. While the reference teaches that NiMo is known, this reference does not
21 directly teach or exemplify Cu and Cr. Examples therein use sulfided NiMo/ Al_2O_3 .

22 **[0007]** US Patent Application No. 20070175795 claims a catalyst for
23 deoxygenation based on a sorbent formulation with zinc oxide and a promoter oxide

1 in reduced state including chromium and copper. However, the formulation therein is
2 distinct from the present invention. While the process of US '795 describes a process
3 wherein a promoter metal is selected from the group consisting of nickel, cobalt, iron,
4 manganese, tungsten, silver, gold, copper, platinum, zinc, tin, ruthenium,
5 molybdenum, antimony, vanadium, iridium, chromium, and palladium, the reference
6 suggests, but does not teach with any specificity, a promoter metal being copper or
7 chromium.

8 [0008] U.S. Patent No. 8,043,600 mentions Group VIB (Group 6) and VIII in
9 its specification for use as catalysts for hydrotreating natural oils. Again, the reference
10 does not teach with any specificity a promoter metal being copper or chromium.

11
12 BRIEF SUMMARY

13 [0009] The present invention is related to catalyst formulations and their use
14 in a fixed bed continuous process to provide superior oxygen removal performance
15 versus conventional hydrotreating catalysts in Step 1 of the above process.

16 [0010] These catalysts contain Mo and at least one selected from Ni and Co as
17 their main (typical) active components, and are promoted with oxides of Cr, Cu, and
18 mixtures thereof. These metal oxide promoters are not normally present in
19 conventional commercial hydrotreating catalysts. These formulations provide
20 unexpectedly superior oxygen removal activity at the same operating conditions as
21 other prior art metal promoters.

1 BRIEF DESCRIPTION OF THE DRAWINGS

2 [0011] Fig. 1 shows oxygen removal as a function of temperature between
3 inventive catalysts and comparative catalysts with no promoters.

4 [0012] Fig. 2 is a graph showing the effect on residual oxygen content of Cr
5 addition to a commercial NiMo catalyst.

6 [0013] Fig. 3 shows oxygen removal as a function of temperature between
7 inventive catalysts and comparative catalysts.

8 [0014] Fig. 4 shows hydrocarbon product selectivities for the inventive and
9 comparative catalysts at 100% oxygen conversion.

10

11 DETAILED DESCRIPTION

12 [0015] The present invention is described with reference to embodiments of
13 the invention. Throughout the description of the invention, reference is made to
14 graphs illustrated in Figs. 1-4.

15 [0016] Renewable diesel fuel can be made from natural oils and greases in a
16 two-step process: Step (1) deoxygenation via catalytic hydrotreating to form n-
17 paraffins with the removal of oxygen as H₂O and/or CO/CO₂ and Step (2)
18 isomerization/cracking of the n-paraffins formed in Step 1 to produce branched diesel
19 and jet fuel products.

20 [0017] As used herein, natural oils and greases are those selected from or
21 derived from animal fats, plant or algae matter, and are often referred to as renewable
22 oils. Natural oils are not based on petroleum or other fossil fuel sources. The

1 renewable oils that can be used in the present invention include any of those which
2 comprise oxygen-containing compounds such as glycerides, fatty acid alkyl esters and
3 free fatty acids (FFA). These oxygen-containing components may be converted to
4 hydrocarbons when contacted with the catalyst under suitable reaction conditions as
5 described in US Patent No. 4,992,605. Examples of these feedstocks include, but are
6 not limited to, canola oil, corn oil, soy oils, rapeseed oil, soybean oil, colza oil, tall oil,
7 sunflower oil, hempseed oil, olive oil, linseed oil, coconut oil, castor oil, peanut oil,
8 palm oil, mustard oil, cottonseed oil, tallow, yellow and brown greases, lard, train oil,
9 fats in milk, fish oil, algal oil, sewage sludge, cuphea oil, camelina oil, jatropha oil,
10 curcas oil, babassu oil, palm kernel oil, crambe oil, and the like. Biorenewable is
11 another term used to describe these feedstocks.

12 **[0018]** As can be appreciated, the renewable oils do not necessarily have to be
13 naturally occurring, but may be derivatives such as the above-noted fatty acid alkyl
14 esters. Such fatty acid alkyl esters can be produced when triglyceride feedstock is
15 contacted with alcohol in the presence of transesterification catalyst and conditions to
16 produce a fatty acid alkyl ester. The alcohol added to the reactor can be one or a
17 mixture of two or more alcohols conventionally used to convert triglyceride-
18 containing feedstocks to esters. Suitable alcohols include those having one to six
19 carbons, and typically are monoalcohols. Methanol is frequently suitable, but the
20 alcohol can include higher monoalcohols such as ethanol, 1-propanol, isopropanol, 1-
21 butanol, isobutanol, 1-pentanol or 1-hexanol.

22 **[0019]** The molar ratio of alcohol to triglyceride in a transesterification
23 reaction is generally in the range of 3:1 to 30:1, and typically in the molar ratio of

1 from 5:1 to 25:1. A molar ratio of alcohol to triglycerides less than 3:1 is more likely
2 to lead to less than stoichiometric conversion of triglyceride to fatty acid alkyl esters.
3 Higher molar ratios of alcohol to triglycerides greater than 30:1 are disadvantageous
4 because the presence of increasing amounts of methanol leads to a much higher cost
5 for separation/recycling of the methanol in the downstream processing steps. The
6 selected molar ratio of alcohol to triglycerides in the above range thus represents an
7 economically sensible ratio, outside of which the conversion can no longer be
8 expected when using other conditions described herein, or when using other
9 conditions conventionally used in reactions of the type described herein.

10 **[0020]** The catalyst used in the transesterification reaction can be a
11 homogeneous or heterogeneous catalyst. Suitable homogeneous catalysts include
12 alkali methoxide, alkali hydroxides and mixtures thereof, including but not limited to,
13 sodium methoxide, potassium methoxide, sodium hydroxide, and potassium
14 hydroxide. Suitable heterogeneous catalysts include those described in US Patents
15 WO 2006/050925; US 2009/0069586; US 5,908,946; WO 2007/025360; or US
16 7,420,073, the contents of which are incorporated herein by reference.

17 **[0021]** The ester derivative produced depends on the number of carbons in the
18 alcohol. Frequently, methanol is used in the transesterification reaction and reactions
19 using methanol produce fatty acid methyl esters, also known as FAME. Ethyl, propyl,
20 butyl, pentyl, and hexyl esters are produced, respectively, when ethanol, propanol,
21 butanol, pentanol, and hexanol are used in the transesterification reaction.

22 **[0022]** The transesterification reaction is carried out in the presence of the
23 catalyst under conventional conditions. The reaction can be carried out in batch

1 reactors, in a continuous (e.g. stirred) tank reactor, as well as in fixed-bed reactors.
2 The reactor conditions should be those sufficient to convert the triglycerides to esters
3 using transesterification. The conditions (also referred to as transesterification
4 conditions) include a temperature in the range of 40 °C to 250 °C, more typically in
5 the range of 60 to 200 °C. Typical pressures would be in the range of 1 to 100
6 atmospheres (atm), more typically 1 to 50 atm, with the final pressure dependent on
7 the specific alcohol and the reaction temperature used in the reaction.

8 **[0023]** The glycerides, FFAs, and fatty acid alkyl esters of the typical
9 vegetable oil or animal fat contain aliphatic hydrocarbon chains in their structure
10 which have about 8 to about 24 carbon atoms with a majority of the oils containing
11 high concentrations of fatty acids with 16 and 18 carbon atoms. The oxygen level in
12 the feedstock for natural oils can range from 0.5 to 20 wt% and more typically from 5
13 to 15 wt%. The feedstocks may contain trace amounts of impurities such as P, Na, Ca,
14 Mg and K originating from the phospholipids, a naturally occurring group of
15 compounds in the oils. These impurities adversely affect the performance of the
16 deoxygenation process and have to be removed to ppm levels prior to this step.
17 Typical pretreatment processes employed for this purpose include but are not limited
18 to low temperature batch processes using solid adsorbents such as silica gel (as
19 described in US Patent No. 5,231,201), ion exchange resins (as described in US
20 Patent Application No. 20060264684) and clays, and the use of guard reactors using
21 hydrotreating type catalysts operating at higher temperatures that are well known in
22 the hydrotreating art. The feedstock can also contain small amounts of nitrogen
23 compounds derived from animal proteins or chlorophyll. The nitrogen content
24 typically ranges from 0.5 ppm to 5000 ppm. Additional optional pretreatment steps

1 comprising the use of a guard reactor operating under hydrotreating conditions may
2 also be employed to saturate the unsaturated fatty acid components of the feedstock to
3 prevent side reactions such as polymerization in the deoxygenation step, as discussed
4 in US Patent Application No. 20110245551.

5 **[0024]** Mixtures or co-feeds of renewable feedstocks and fossil fuel derived
6 hydrocarbons may also be used as the feedstock.

7 **[0025]** The deoxygenation of the natural oils and greases to form n-paraffins
8 is carried out using a single or multi-layer catalytic bed approach. During the
9 deoxygenation process, the fatty acid chains in the triglycerides are converted to n-
10 paraffins whereas the glyceride portion of the triglycerides is converted to propane.
11 Typically, the hydrocarbon product distribution from the deoxygenation of natural
12 oils shows a mixture of even and odd carbon number n-paraffins with the even
13 carbons produced via the removal of oxygen as water and the odd carbons produced
14 via the removal of oxygen as CO or CO₂). Higher selectivity to even numbered
15 paraffins indicates higher retention of carbon in the diesel product and is tied to a
16 greater consumption of hydrogen. Higher selectivity to odd numbered paraffins is tied
17 to lower hydrogen consumption and with a lower retention of carbon in the diesel
18 product.

19 **[0026]** Typically, the deoxygenation process uses sulfided hydrotreating type
20 catalysts. Other catalysts based on precious metals such as Pd may also be used to
21 provide higher selectivity towards the removal of oxygen as CO and CO₂ and to
22 minimize H₂ consumption as described in US Patent No. 7,491,858. The present
23 invention is tied to deoxygenation processes using sulfided catalysts.

1
2 **[0027]** Normally the catalytic bed is a fixed bed of pellets or extrudates, which
3 is operated either in trickle (downflow) mode or flooded bed (upflow) mode under
4 applied hydrogen pressure and elevated temperature. Typically, the natural oils and
5 greases are also spiked with small quantities of an organic sulfur compound such as
6 dibutyl disulfide commercially available as SULFRZOL (Lubrizol Corporation) to
7 ensure that the active site on the catalyst stays in the sulfided state during reaction. In
8 addition to H₂O, CO CO₂ and propane, the gas portion of the products also contains
9 H₂S formed during desulfurization reactions. In the case of reactions with animal fat
10 or other nitrogen-containing feedstocks, the gas products may also contain NH₃
11 formed via denitrogenation reactions.

12 **[0028]** In a commercial process, the deoxygenation step is followed by a
13 product separation step to remove the gaseous products from the liquid diesel product
14 prior to the hydroisomerization or hydrocracking step. The deoxygenation step is
15 typically carried out in the presence of excess of hydrogen beyond the
16 stoichiometrically required amount, possibly up to two to three times the excess. The
17 process can also encompass recycle of product and gases to improve the heat balance
18 in the reactor.

19 **[0029]** The suitable catalysts for the deoxygenation process in the present
20 invention are those on which catalytic metals are provided on a support predominantly
21 comprised of alumina, typically extruded gamma alumina with a BET surface area of
22 at least 150 m²/g and a pore volume of at least 0.5 cc/g. However, the support can
23 comprise any suitable material having sufficient strength and porosity to function as a
24 support. The catalyst can be in a granulated form (granules, beads, spheres, tablets,

1 and extrudates), for example, those appropriate for use in a fixed bed reactor designed
2 for continuous operation. The granulated forms can have dimensions in the range of
3 0.1 to 10 mm, and more typically, in the range of 0.5 to 5 mm. The form can be of any
4 shape, for example, cylindrical, trilobe or quadrulobe. The granulation process can be
5 a combination of mixing and extrusion. The formulation for the extruder feed may
6 optionally comprise other oxides in addition to alumina, such as SiO_2 , TiO_2 and ZrO_2 ,
7 MgO or clays. The oxides can modify the pore characteristics and/or mechanical
8 strength of the final support (measured as crush strength). Extrusion aids such as
9 methyl cellulose (for example, commercially available as METHOCEL (Dow
10 Chemical Company)) may also be used to improve the processing of the feed through
11 the extruder. Optionally acids such as nitric acid may be added for peptization of the
12 alumina or other oxides to form a binder, thereby enhancing mechanical strength to
13 the granulated material. The inorganic oxide or oxides can be added in any form to the
14 mixing equipment, as a slurry, a peptizable solid, or a liquid. Aluminum oxide,
15 aluminum hydroxide, silicon dioxide, titanium dioxide and zirconium oxide are
16 typically added or processed as solids. Aluminum nitrate, aluminum hydroxide, tetra
17 ethyl ortho silicate (TEOS), titanium isopropoxide and zirconyl nitrate are typical
18 liquid forms of materials added to the mixing equipment. Colloidal forms, such as
19 colloidal silica can also be used. The inorganic oxides can be added to the equipment
20 as separate ingredients or as a mixed oxide, wherein the mixed oxide is prepared
21 using techniques including but not limited to co-precipitation.

22 **[0030]** In addition, the water level is adjusted to optimize the extrudability of
23 the catalyst. The formulation forming the extruder feed is first mixed in a mixer for
24 example, Sigma or Eirich mixer and is then extruded through a commercially

1 available single screw or twin screw extruder. The extruded material is then dried and
2 calcined to form the finished catalyst. Granulated particle embodiments are typically
3 calcined during the forming process at temperatures from 500 °F to 2000 °F, more
4 preferably from 700 °F to 1800 °F and most preferably from 900 °F to 1600 °F. The
5 catalyst can also be granulated into a spherical form with similar ingredients
6 mentioned above, but done so in a Eirich or a Naute Mixer, followed by similar
7 drying/calcination processes.

8 **[0031]** Catalyst metal compounds provided on the support are based on Mo, at
9 least one selected from Ni and Co, and include at least one promoter metal being at
10 least one selected from Cu and Cr. It is this specific promoter metal that, in
11 combination with MoNi, MoCo or MoNiCo, provides the superior deoxygenation
12 activity of the present catalysts.

13 **[0032]** The promoter metal selected from the group consisting of Cu and Cr is
14 contained in the catalyst in an amount sufficient to significantly enhance
15 deoxygenation of the natural oils and greases. The amount of the promoter in the
16 catalyst calculated as oxide is preferably in the 0.5 to 10 wt% range, more preferably
17 in the 1 wt% to 6 wt% range and most preferably in the 1.5 to 5.0 wt% range.

18 **[0033]** The promoter metals along with the base Ni, Mo, Co metals can be
19 incorporated onto the extrudate support using standard impregnation techniques
20 known in the art, for example incipient wetness impregnation of solutions containing
21 precursors of the active metals. These precursors include, but are not limited to,
22 nitrates, carbonates, oxalates etc. The impregnation step is typically followed by
23 drying and calcination steps to convert the promoter metal precursor to the oxide

1 form. Drying is typically carried out in the temperature range of 200 °F to 400 °F.
2 Final calcinations are typically carried out in the temperature range of 500 °F to 2000
3 °F, more preferably from 700 °F to 1800 °F and most preferably from 900 °F to 1600
4 °F.

5 **[0034]** Optionally, a portion or all of these promoter metals could also be
6 added during the mixing step of the catalyst preparation process and can be added in
7 any form including but not limited to metal solutions.

8 **[0035]** The catalysts are prepared as oxides during the manufacturing process
9 and subsequently converted to the active sulfided state either with *in situ* or *ex situ*
10 activation procedures. Part or most of these metal oxide formulations could be
11 converted to the sulfided state during the activation step. The activation step is
12 typically carried out by exposing the catalyst to one or more sulfur containing
13 compounds and hydrogen with a controlled ramp of reactor temperature from about
14 70 °F to about 650 °F.

15 **[0036]** Exceptional deoxygenation results are achieved when deoxygenation is
16 effected by exposing natural oils or greases to the catalyst at a catalyst temperature
17 preferably between about 400 °F to about 800 °F, more preferably between 450 and
18 700 °F and most preferably between 500 and 650 °F. The operating pressures are
19 preferred to be about 100 to 2500 psig, more preferably about 250 to 2000 psig and
20 most preferably about 400 to 1500 psig. The processing rates of feedstocks used for a
21 catalytic process can be expressed for example as Liquid Hourly Space Velocity
22 (LHSV) defined as the volumetric flow rate of the reactant divided by volume of
23 active catalyst in the reactor. The LHSV for our process can range from 0.1 to 10 h⁻¹,

1 more preferably 0.2 to 5.0 h⁻¹ and most preferably 0.5 to 2.0 h⁻¹. Hereinafter, the
2 present invention will be described in more detail with reference to Examples.
3 However, the scope of the present invention is not limited to the specific details set
4 forth in the following Examples.

5 [0037] Materials used for screening in the examples: NiMoP/Al₂O₃-SiO₂
6 catalysts promoted with 2.0-4.7 wt% Cr₂O₃, 1.9 wt% CuO, 3.4% Fe₂O₃ and 3.8%
7 ZnO.

8

9

EXAMPLE 1

10 [0038] Synthesis of chromium-promoted NiMoP catalyst (Catalyst A)

11 [0039] A mixed metal solution of NiMo was prepared as follows. Pre-weighed
12 amounts of water, phosphoric acid (75 wt%), molybdenum trioxide and basic nickel
13 carbonate (40 wt% Ni) were added to a kettle and heated to 200 °F with stirring. The
14 mixture was cooked at 200 °F for 3 hours or until the solution was clear. Water
15 addition was performed as needed to compensate for any loss due to evaporation. The
16 mixture was subsequently cooled to room temperature. To 65 ml of this precursor
17 solution, 18.6 g of chromium nitrate nonahydrate and 35 ml of water was added. This
18 solution mixture was impregnated onto 99 g of an alumina-silica extrudate support
19 (1/16" asymmetric quadrulobes) to incipient wetness. The impregnated catalyst was
20 then dried at 248 °F overnight followed by calcination at 1112 °F for 1 hour in a
21 muffle furnace. The resulting catalyst is denoted as Catalyst A and contains 23.2%
22 MoO₃, 5.0% NiO, 3.4% P₂O₅, 2.2 wt% SiO₂ and 2.0 wt% Cr₂O₃ with a BET surface
23 area of 209 m²/g.

EXAMPLE 2

[0040] Synthesis of chromium-promoted NiMoP catalyst (Catalyst B)

[0041] A mixed metal solution of NiMo was prepared as follows. Pre-weighed amounts of water, phosphoric acid (75 wt%), molybdenum trioxide and basic nickel carbonate (40 wt% Ni) were added to a kettle and heated to 200 °F with stirring. The mixture was cooked at 200 °F for 3 hours, or until the solution was clear. Water addition was performed as needed to compensate for any loss due to evaporation. The mixture was subsequently cooled to room temperature. To 65 ml of this precursor solution, 37.2 g of chromium nitrate nonahydrate and 25 ml of water was added. This solution mixture was impregnated onto 99 g of an alumina-silica extrudate support (1/16" asymmetric quadrulobes) to incipient wetness. The impregnated catalyst was then dried at 248 °F overnight followed by calcination at 1112 °F for 1 hour in a muffle furnace. The resulting catalyst is denoted as Catalyst B and contains 20.4% MoO₃, 5.2% NiO, 3.4% P₂O₅, 2.6 wt% SiO₂ and 4.1 wt% Cr₂O₃ with a BET surface area of 207 m²/g.

EXAMPLE 3

[0042] Synthesis of copper-promoted NiMoP catalyst (Catalyst C)

[0043] A mixed metal solution of NiMo was prepared as follows. Pre-weighed amounts of water, phosphoric acid (75 wt%), molybdenum trioxide and basic nickel carbonate (40 wt% Ni) were added to a kettle and heated to 200 °F with stirring. The mixture was cooked at 200 °F for 3 hours, or until the solution was clear. Water addition was performed as needed to compensate for any loss due to evaporation. The mixture was subsequently cooled to room temperature. To 65 ml of this precursor

1 solution, 37.2 g of copper nitrate trihydrate and 25 ml of water was added. This
2 solution mixture was impregnated onto 99 g of an alumina-silica extrudate support
3 (1/16" asymmetric quadrulobes) to incipient wetness. The impregnated catalyst was
4 then dried at 248 °F overnight followed by calcination at 1112 °F for 1 hour in a
5 muffle furnace. The resulting catalyst is denoted as Catalyst C and contains 23.8%
6 MoO₃, 4.8% NiO, 3.7% P₂O₅, 2.4 wt% SiO₂ and 1.9 wt% CuO with a BET surface
7 area of 182 m²/g.

8 COMPARATIVE EXAMPLE 1

9 [0044] The reference catalyst used in this case was a commercial NiMoP
10 hydroprocessing catalyst received from Advanced Refining Technologies made via
11 impregnation of NiMoP precursor solution onto the same support. The reference
12 catalyst contains 27.3% MoO₃, 5.4% NiO, 4.3% P₂O₅, and 2.1 wt% SiO₂ with a BET
13 surface area of 170 m²/g and is designated as Catalyst D.

14 EXAMPLE 4

15 [0045] Synthesis of chromium-promoted NiMoP catalyst (Catalyst E)

16 [0046] Catalyst E was prepared as follows. A chromium solution was
17 prepared by dissolving 30 g of chromium nitrate nonahydrate in 60 ml water. This
18 solution was impregnated onto 97 g of Catalyst D. The impregnated catalyst was dried
19 at 248 °F overnight followed by calcination at 1112 °F for 1 hour in a muffle furnace.
20 The resulting catalyst contained 25% MoO₃, 5.4% NiO, 4.1% P₂O₅, 2.2 wt% SiO₂ and
21 4.7 wt% Cr₂O₃ with a BET surface area of 177 m²/g.

22

COMPARATIVE EXAMPLE 2

[0047] Synthesis of iron-promoted NiMoP catalyst (Catalyst F)

[0048] A mixed metal solution of NiMo was prepared as follows. Pre-weighed amounts of water, phosphoric acid (75 wt%), molybdenum trioxide and basic nickel carbonate (40 wt% Ni) were added to a kettle and heated to 200 °F with stirring. The mixture was cooked at 200 °F for 3 hours or until the solution was clear. Water addition was performed as needed to compensate for any loss due to evaporation. The mixture was subsequently cooled to room temperature. To 65 ml of this precursor solution, a solution prepared by the separate dissolution of 24 g of iron nitrate nonahydrate in 20 ml of water was added. This solution mixture was impregnated onto 99 g of an alumina-silica extrudate support (1/16" asymmetric quadrulobes) to incipient wetness. The impregnated catalyst was then dried at 248 °F overnight followed by calcination at 1112 °F for 1 hour in a muffle furnace. The resulting catalyst is denoted as Catalyst F and contains 27.9% MoO₃, 4.5% NiO, 4.1% P₂O₅, 2.0 wt% SiO₂ and 3.4 wt% Fe₂O₃ with a BET surface area of 201 m²/g.

COMPARATIVE EXAMPLE 3

[0049] Synthesis of zinc-promoted NiMoP catalyst (Catalyst G)

[0050] A mixed metal solution of NiMo was prepared as follows. Pre-weighed amounts of water, phosphoric acid (75 wt%), molybdenum trioxide and basic nickel carbonate (40 wt% Ni) were added to a kettle and heated to 200 °F with stirring. The mixture was cooked at 200 °F for 3 hours, or until the solution was clear. Water addition was performed as needed to compensate for any loss due to evaporation. The mixture was subsequently cooled to room temperature. To 58 ml of this precursor

1 solution, a solution prepared by the separate dissolution of 22 g of zinc nitrate
2 hexahydrate in 42 ml of water was added. This solution mixture was impregnated
3 onto 99 g of an alumina-silica extrudate support (1/16" asymmetric quadrulobes) to
4 incipient wetness. The impregnated catalyst was then dried at 248 °F overnight
5 followed by calcination at 1112 °F for 2 hours in a muffle furnace. The resulting
6 catalyst is denoted as Catalyst G and contains 28.7% MoO₃, 5.7% NiO, 4.3% P₂O₅,
7 2.4 wt% SiO₂ and 3.8 wt% ZnO with a BET surface area of 100 m²/g. The
8 significantly lower surface area of Catalyst G also suggests a sintering effect of ZnO
9 addition to the catalyst formulation.

10 [0051] Evaluation of Catalysts A-G for deoxygenation of natural oils in a
11 fixed bed reactor.

12 [0052] The performance of Catalysts A-G for oxygen removal from
13 triglycerides was evaluated in a fixed bed reactor in up flow mode. The active catalyst
14 bed was diluted with alpha alumina beads (with very low surface area) for better heat
15 distribution. The catalysts were converted into the active sulfides using kerosene and
16 H₂ with a multistep temperature ramp from room temperature to 630 °F. Subsequently
17 the flow was switched to refined soybean oil spiked with 100 ppmw S (using
18 SULFRZOL - dibutyl disulfide) along with H₂. The conditions used were a H₂ : Oil
19 ratio of 5600 SCFB (standard ft³/barrel), Pressure of 750 psia, and a temperature
20 range of 500 to 575 °F. Catalysts A-D, F and G were evaluated at a Weight Hourly
21 Space Velocity of 1.0 h⁻¹ while catalysts D and E were evaluated at a Liquid Hourly
22 Space Velocity of 1.0 h⁻¹ (corresponding approximately to a Weight Hourly Space

1 Velocity of 1.3 h⁻¹). The liquid and gaseous products from the reaction were analyzed
2 using gas chromatography.

3 **[0053]** As can be seen in Fig. 1, Catalysts A-C achieve unexpectedly higher
4 levels of oxygen removal as a function of temperature than the standard Catalyst D.
5 Specifically, at a temperature of 500 °F, Catalyst D showed a baseline of 3.1 wt%
6 residual oxygen. On the other hand, Catalyst B achieved a much lower total oxygen of
7 2.1 wt%, a 33% reduction of residual oxygen compared to the baseline. Catalyst A
8 showed residual oxygen content of 0.97 wt %, a reduction of 69% compared to the
9 baseline Catalyst D. Further, Catalyst C showed residual oxygen content of 0.45 wt%,
10 a reduction of 86% compared to the baseline.

11 **[0054]** Fig. 2 illustrates the significant improvement in oxygen upon addition
12 of Cr to the commercial NiMo catalyst (Catalyst D).

13 **[0055]** As noted above, various promoter metals have previously been used as
14 promoter metals, but it is the specific inclusion of Cu or Cr that promotes the
15 unexpectedly superior deoxygenation results of the inventive catalysts.

16 **[0056]** Fig. 3 shows oxygen removal as a function of temperature between
17 inventive catalysts including Cu and Cr and comparative catalysts including different
18 promoter metals. It can be observed that while Cu and Cr deliver superior oxygen
19 reduction performance compared to the baseline NiMo catalyst, the addition of Fe and
20 Zn has an adverse effect on performance.

21 **[0057]** Importantly, the improvement in deoxygenation activity of the present
22 catalyst is achieved without significant changes in the gas or liquid product
23 selectivities.

1 **[0058]** Fig. 4 shows the hydrocarbon product selectivity for the inventive and
2 comparative catalysts at 100% oxygen conversion. It can be observed that the higher
3 deoxygenation activity for Catalysts A, B, C and E is also accompanied by higher
4 selectivity to even numbered products.

5 **[0059]** The method of deoxygenation of the present invention using catalysts
6 containing Mo and Ni and/or Co as main active components and promoted with
7 oxides of Cr, Cu, and mixtures thereof not normally present in conventional
8 hydrotreating catalysts provide unexpectedly superior oxygen removal activity at the
9 same operating conditions as other prior art metal promoters.

10 **[0060]** The foregoing examples and embodiments were presented for
11 illustrative purposes only and not intended to limit the scope of the invention.
12 Furthermore, although the present invention has been disclosed and described by way
13 of some embodiments, it is apparent to those skilled in the art that several
14 modifications to the described embodiments, as well as other embodiments of the
15 present invention are possible without departing from the scope thereof as defined in
16 the appended claims.

1 We claim:

2 1. A method for deoxygenating renewable oils comprised of natural oils or
3 greases or derivatives thereof comprising triglycerides or free fatty acids, comprising
4 the steps of:

5 providing a catalyst comprising:

6 a support predominantly comprised of alumina,

7 metal compounds provided on the support, the metal compounds based on Mo
8 and at least one selected from the group consisting of Ni and Co, and

9 at least one promoter selected from the group consisting of Cu and Cr;

10 and

11 contacting the renewable oils with the catalyst under conditions sufficient to
12 promote deoxygenation of the renewable oils.

13 2. The method of claim 1, wherein the promoter metal is Cu.

14 3. The method of claim 1, wherein the promoter metal is Cr.

15 4. The method of claim 1, wherein the promoter metal is present in the catalyst
16 formulation in an amount calculated as an oxide between about 1.4 wt% and about 3.0
17 wt%.

18 5. The method of claim 1, wherein the promoter metal is introduced prior to the
19 extrusion stage of the catalyst manufacturing process.

20 6. The method of claim 1, wherein the support comprises at least one additional
21 oxide from the group comprising silica, titania and zirconia.

- 1 7. The method of claim 1, wherein the support comprises silica.
- 2 8. The method of claim 1, wherein the catalyst comprises phosphorus.
- 3 9. The method of claim 1, wherein the renewable oils in the feedstock comprise
4 triglycerides.
- 5 10. The method of claim 1, wherein the renewable oils in the feedstock comprise
6 free fatty acids,
- 7 11. The method of claim 1, wherein the feedstock has been subjected to one or
8 more pretreatment steps to reduce the level of contaminants comprising any of the
9 group consisting of Na, Ca, Fe, Mg, K and P.
- 10 12. The method of claim 1, wherein the step of contacting the renewable oils
11 with the catalyst is performed at a temperature between about 500 °F and 650 °F.
- 12 13. The method of claim 1, wherein the step of contacting the renewable oils
13 with the catalyst is performed at a pressure between about 450 psig and 1500 psig.
- 14 14. The method of claim 1, wherein the step of contacting the renewable oils
15 with the catalyst is performed at a LHSV of 0.5 to 2.0 h⁻¹.

Fig. 1. Oxygen conversion performance of catalysts A-D.

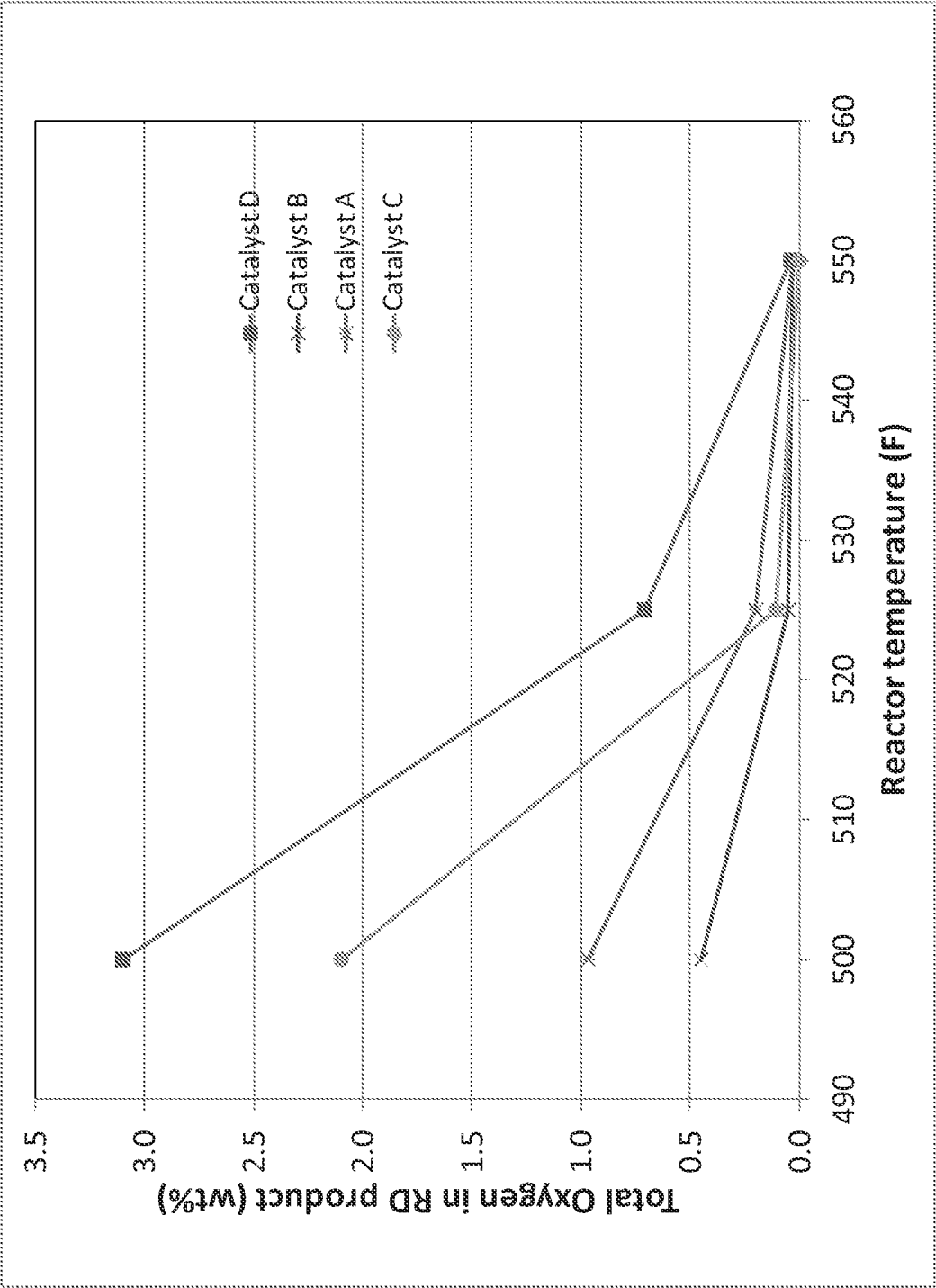


Fig. 2. Oxygen conversion performance of Catalysts D and E.

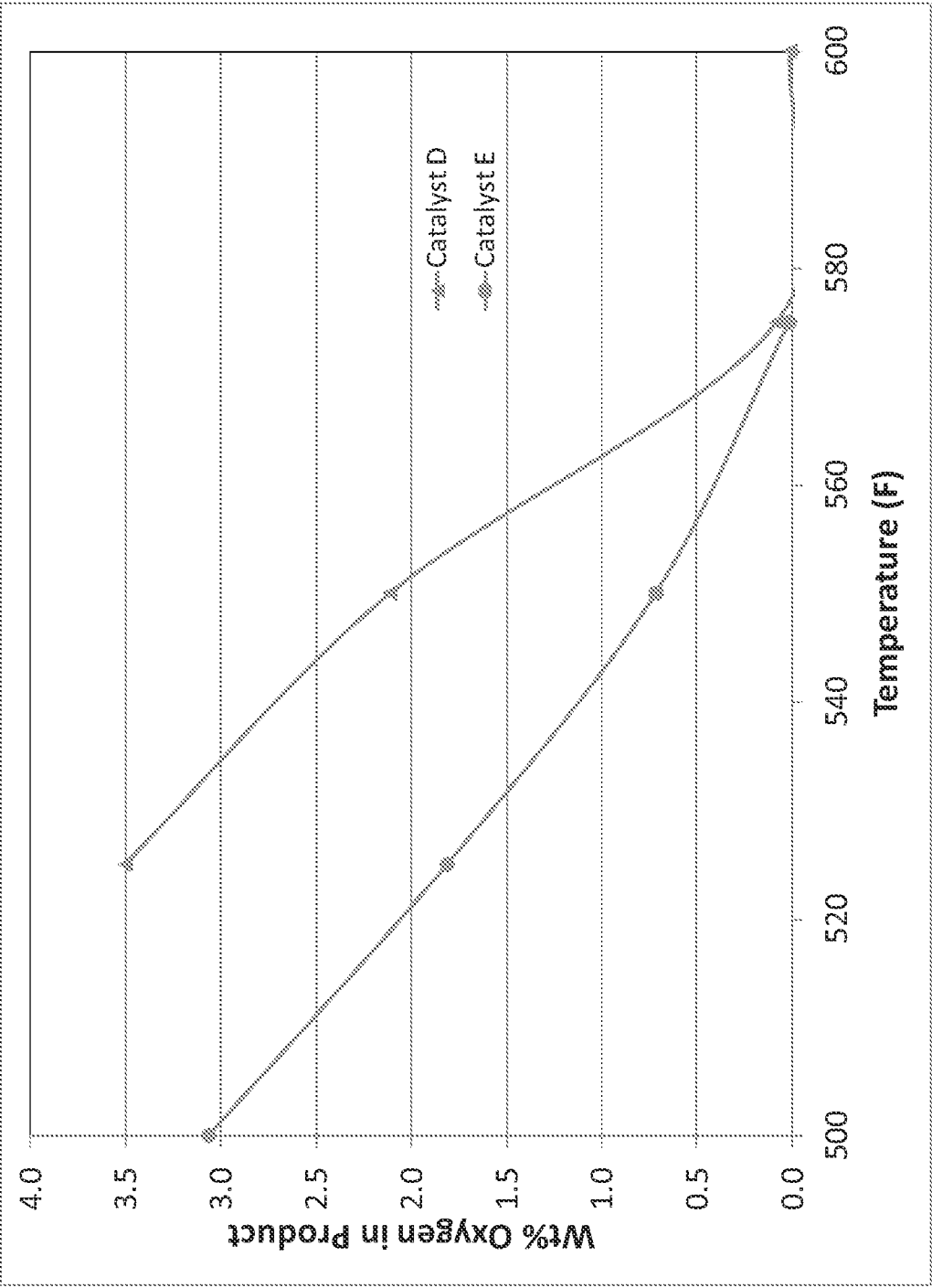


Fig. 3. Oxygen conversion performance of Catalysts B, C, D, F and G.

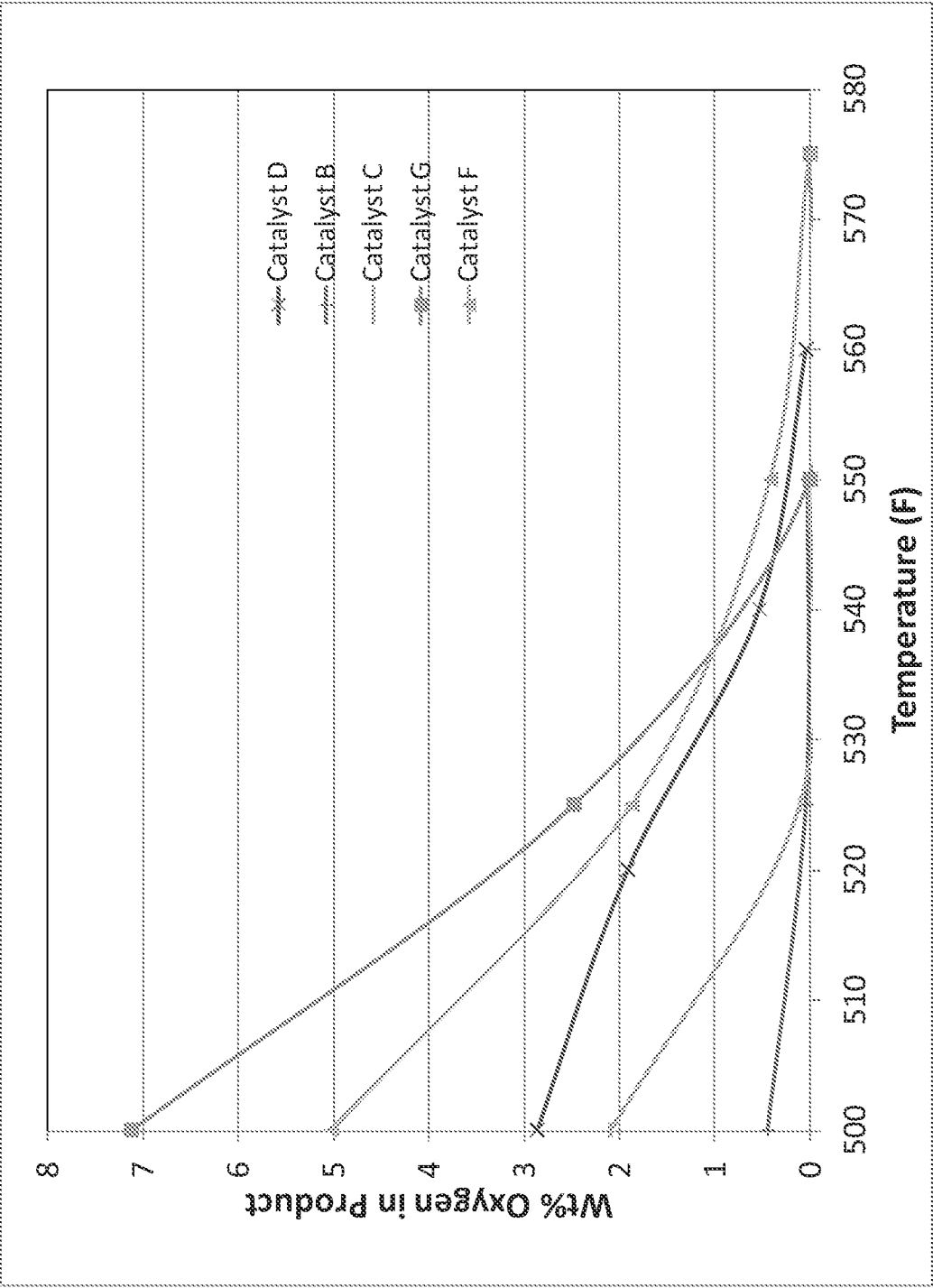
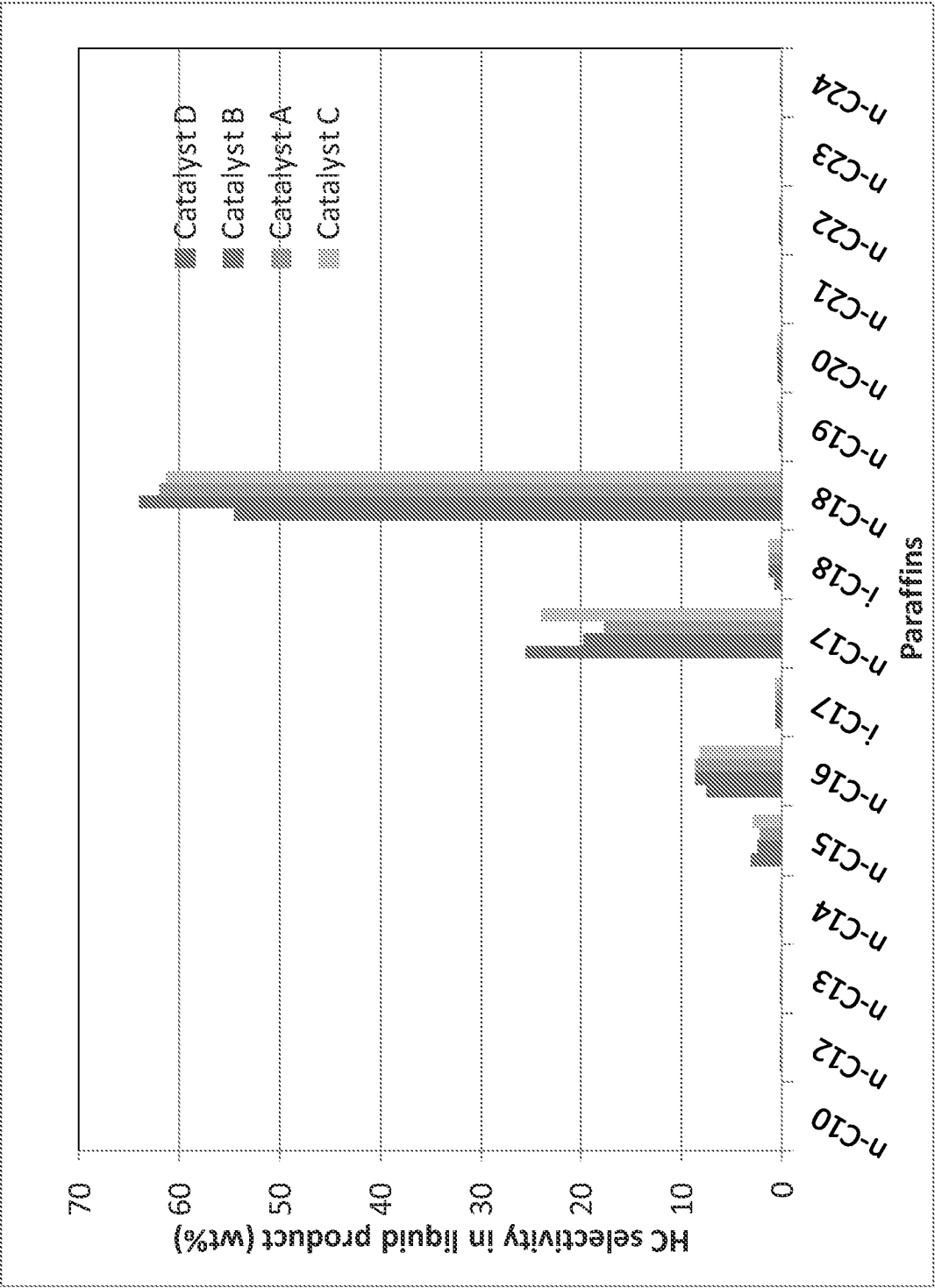


Fig. 4. Hydrocarbon (n-paraffin) product selectivity for catalysts A-D at 100% O conversion at 550 °F.



INTERNATIONAL SEARCH REPORT

International application No.

PCT/US15/34621

A. CLASSIFICATION OF SUBJECT MATTER

IPC(8) - C07C 1/00, 1/02, 1/20, 1/24, 1/213 (2015.01)

CPC - C07C 1/00, 1/02, 1/20, 1/24, 1/213

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

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC(8): C07C 1/00, 1/02, 1/20, 1/24, 1/213 (2015.01)

CPC: C07C 1/00, 1/02, 1/20, 1/24, 1/213

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)

PatSeer (US, EP, WO, JP, DE, GB, CN, FR, KR, ES, AU, IN, CA, INPADOC Data), Google, Google Scholar, ProQuest, IP.com
Keywords: hydrodeoxygenation, vegetable oil, catalyst, promoter, paraffins, biodiesel, hydrotreating, copper, chromium, modifier**C. DOCUMENTS CONSIDERED TO BE RELEVANT**

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US 8,026,401 B2 (ABHARI, R et al.) September 27, 2011; column 2, lines 33-36; column 3, lines 53-58; column 4, lines 26-27; column 5, lines 17-22; column 6, line 46-47, table II; column 7, lines 29-31; claim 5	1-14
Y	US 2013/0143972 A1 (CELANESE INTERNATIONAL CORPORATION) June 6, 2013; paragraphs [0125], [0144]-[0147]	1-14
Y	US 2009/0029850 A1 (KITAMURA, T et al.) January 29, 2009; paragraphs [0008], [0023], [0024]	5

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

* Special categories of cited documents:

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

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

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Date of the actual completion of the international search

06 August 2015 (06.08.2015)

Date of mailing of the international search report

03 SEP 2015

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