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(54) SYSTEMS AND METHODS FOR PRODUCING FUEL INTERMEDIATES

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C10G 3/00	(2006.01)

(52) **U.S. Cl.**

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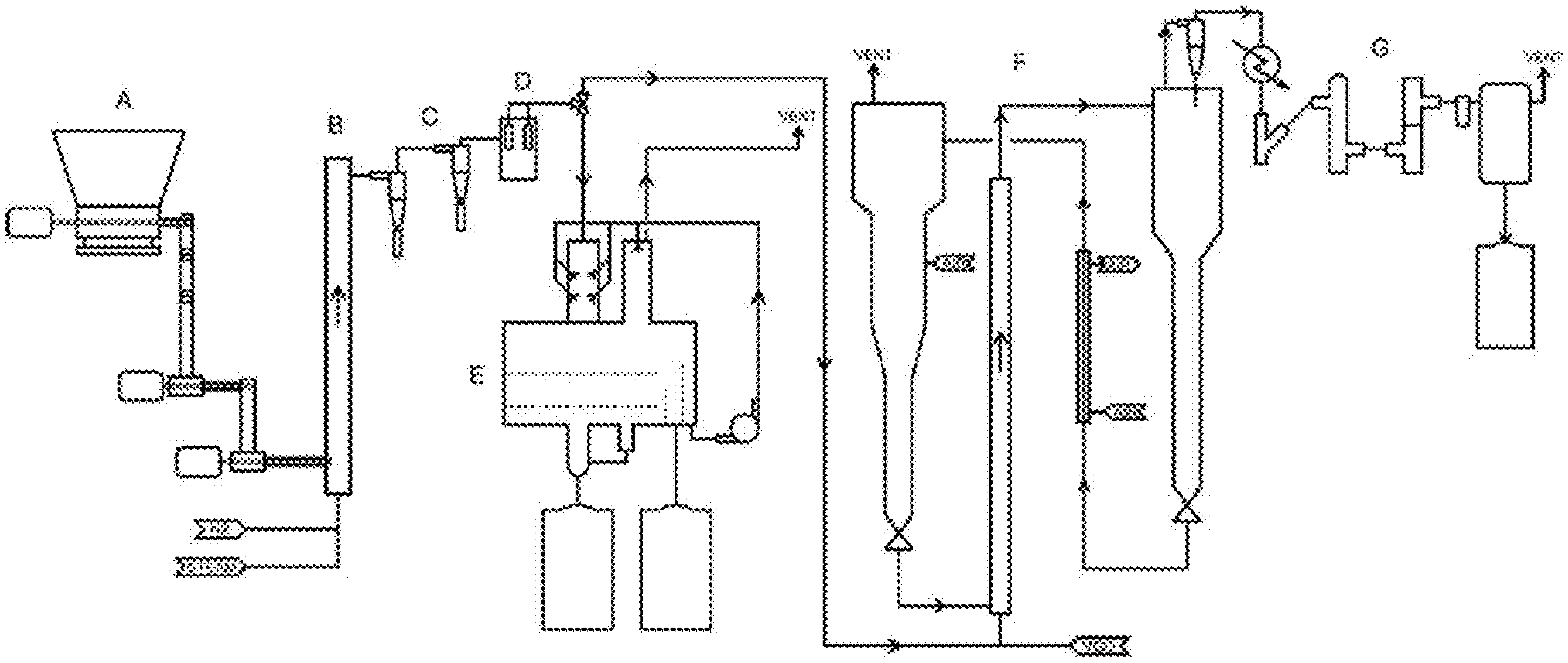
(57) ABSTRACT

The present disclosure relates to a liquid composition that includes an alkane concentration between 40 wt % and 55 wt %, and an alkene concentration between greater than 0 wt % and 20 wt %, where cyclopentenone accounts for greater than 65 wt % of the alkane concentration. In some embodiments of the present disclosure, the liquid composition may further include phenol. In some embodiments of the present disclosure, at least a portion of the liquid composition may be bioderived.



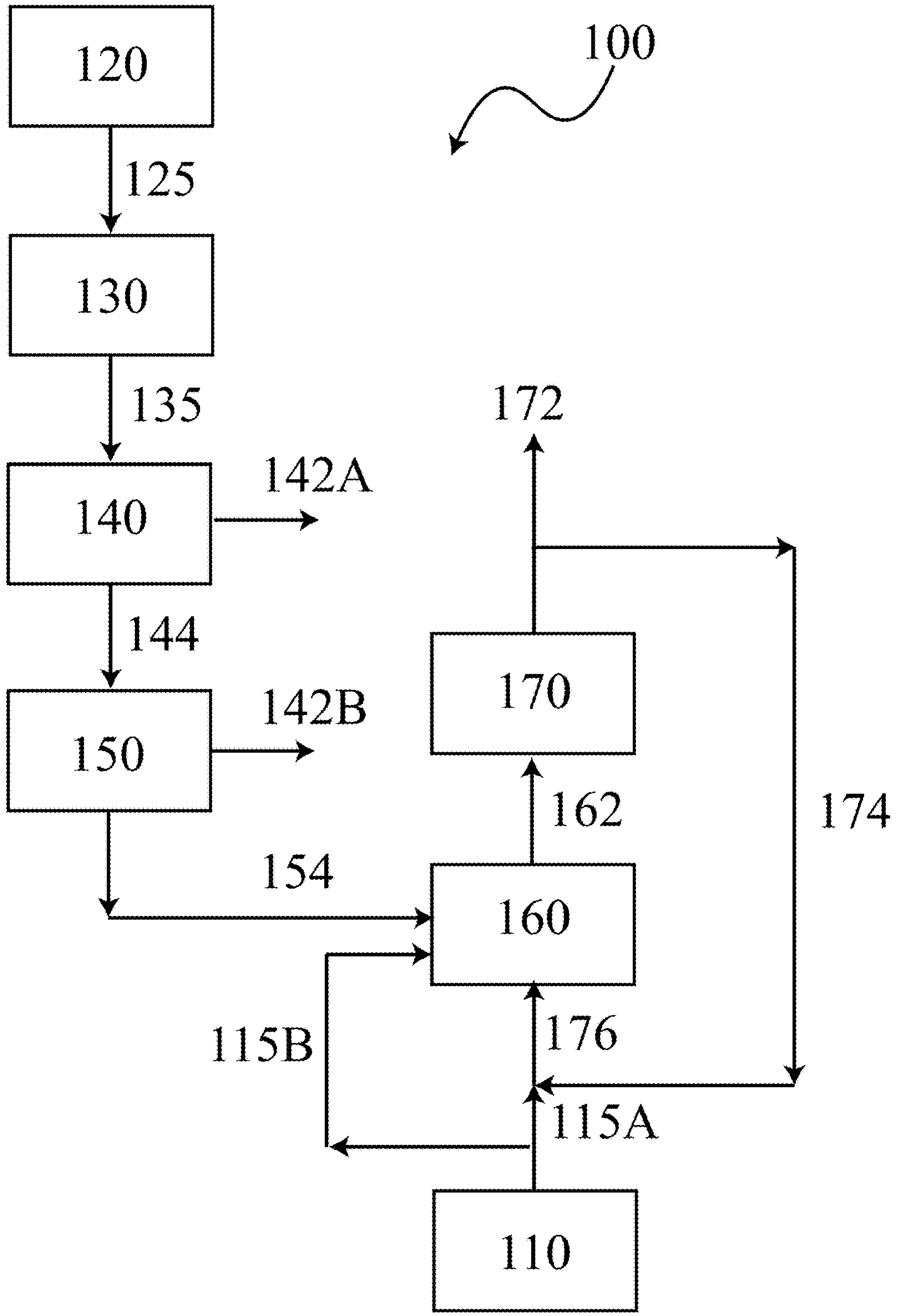

120
100
125
130
135
172
140
142A
144
170
150
142B
162
174
154
160
115B
176
115A
110

Figure 1

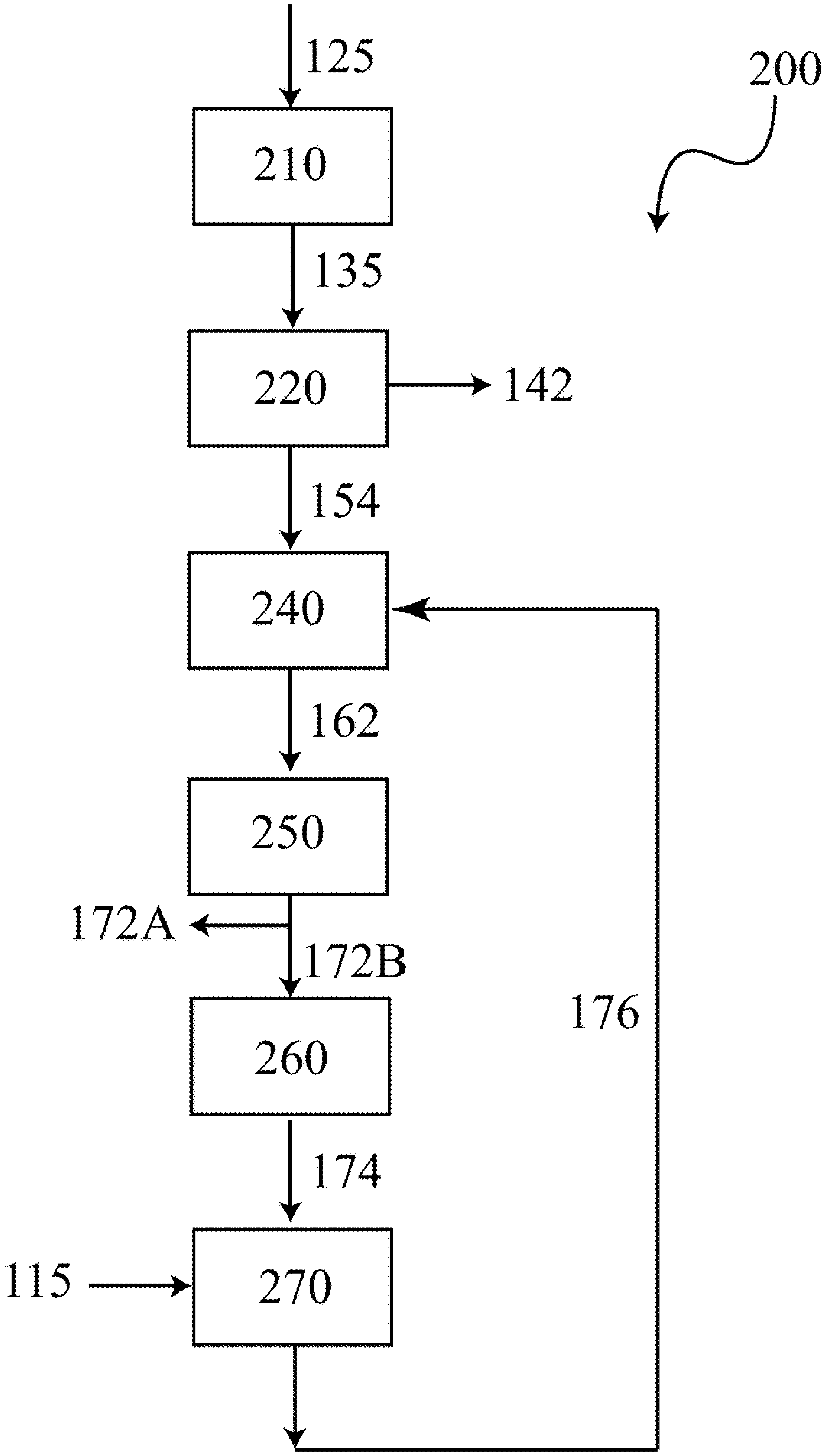

125
200
210
135
220
142
154
240
162
250
172A
172B
260
176
174
115
270

Figure 2

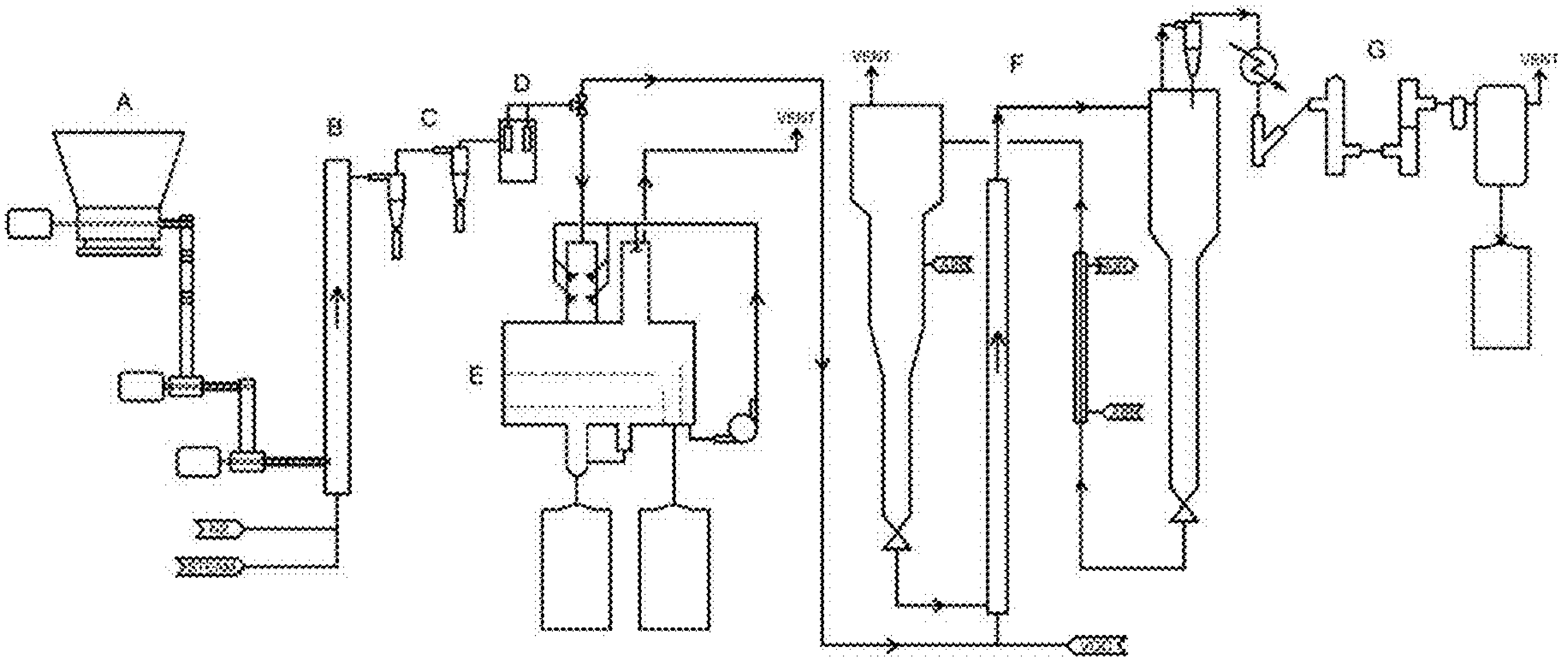


Figure 3

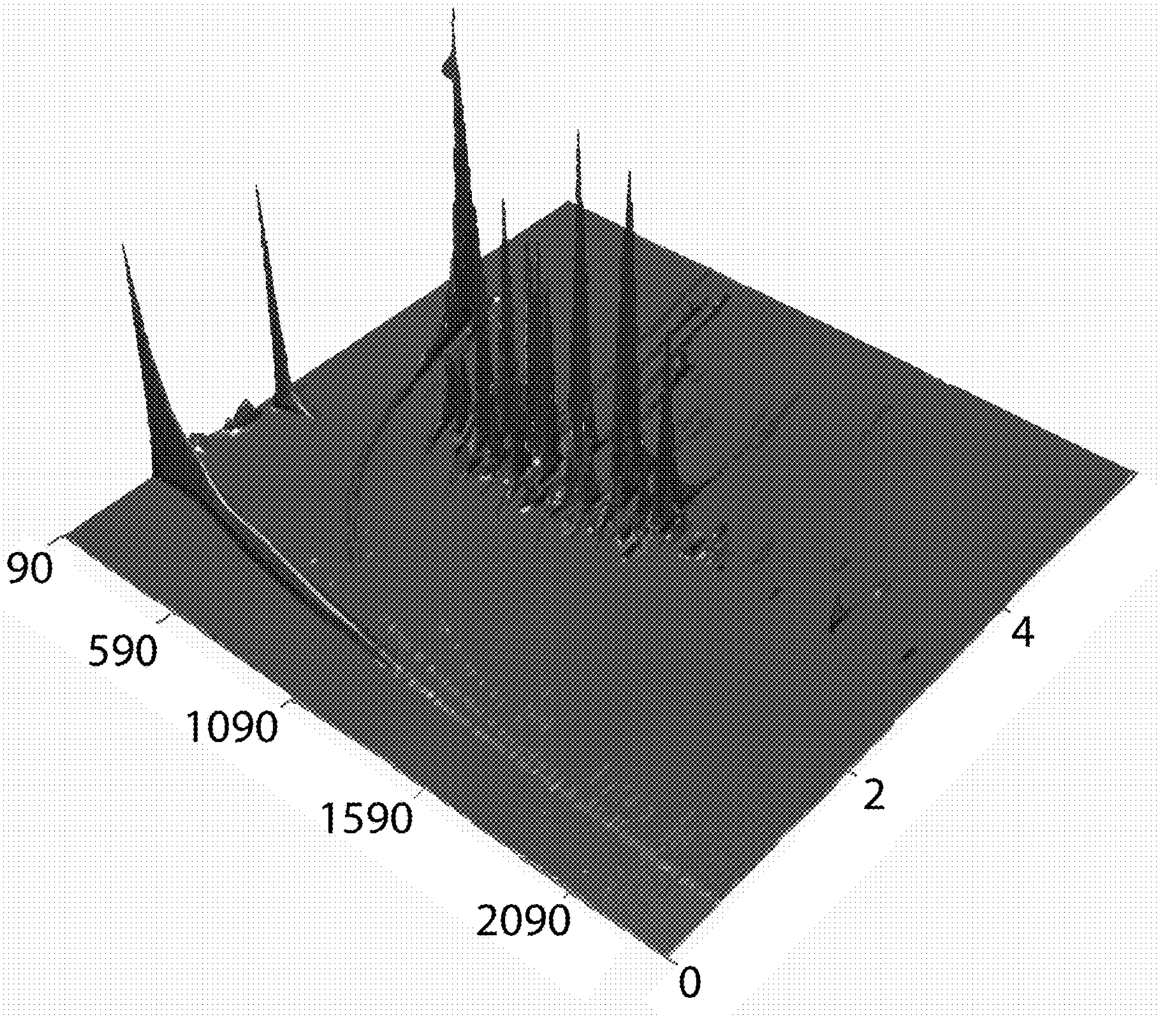


Figure 4A

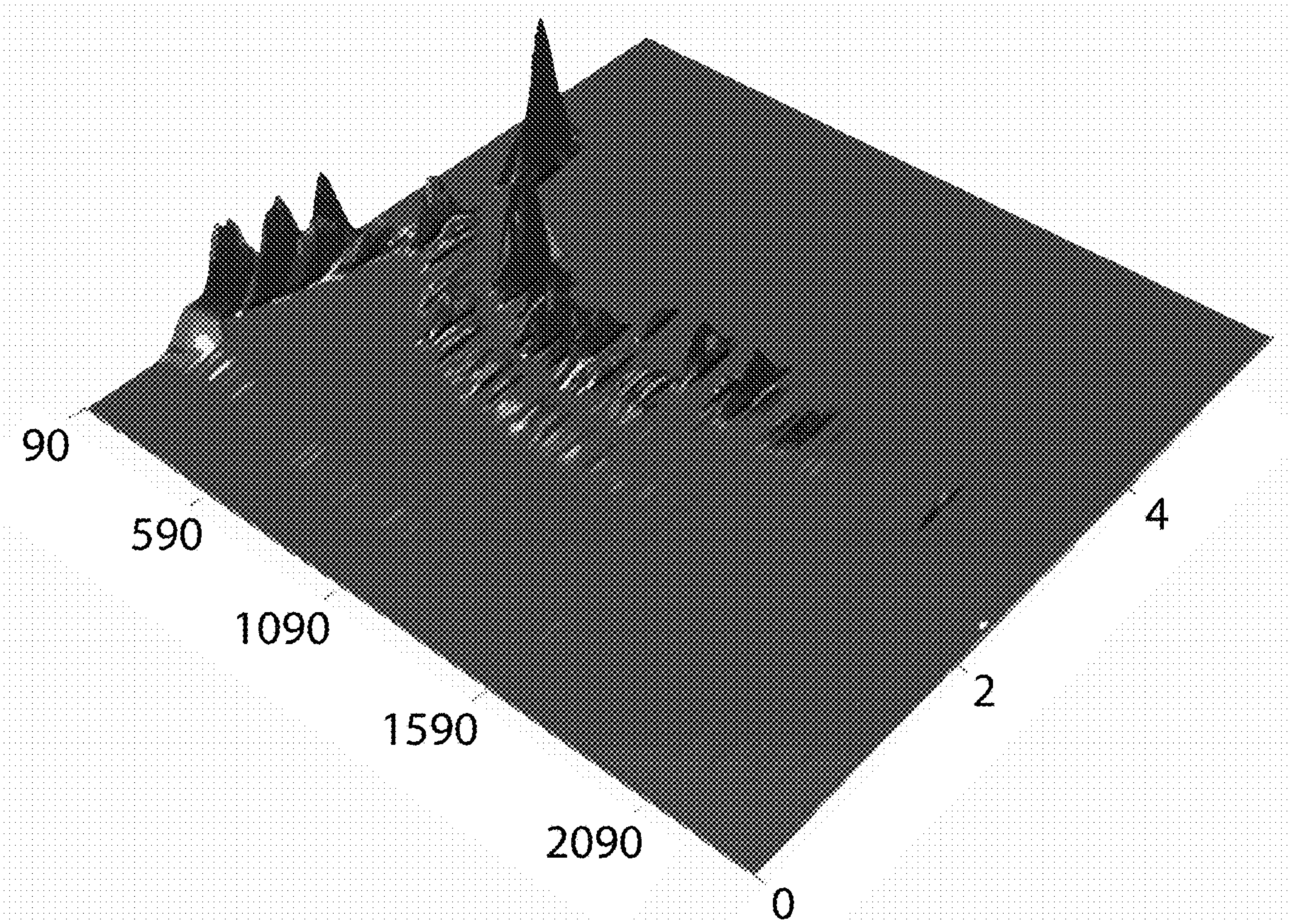


Figure 4B

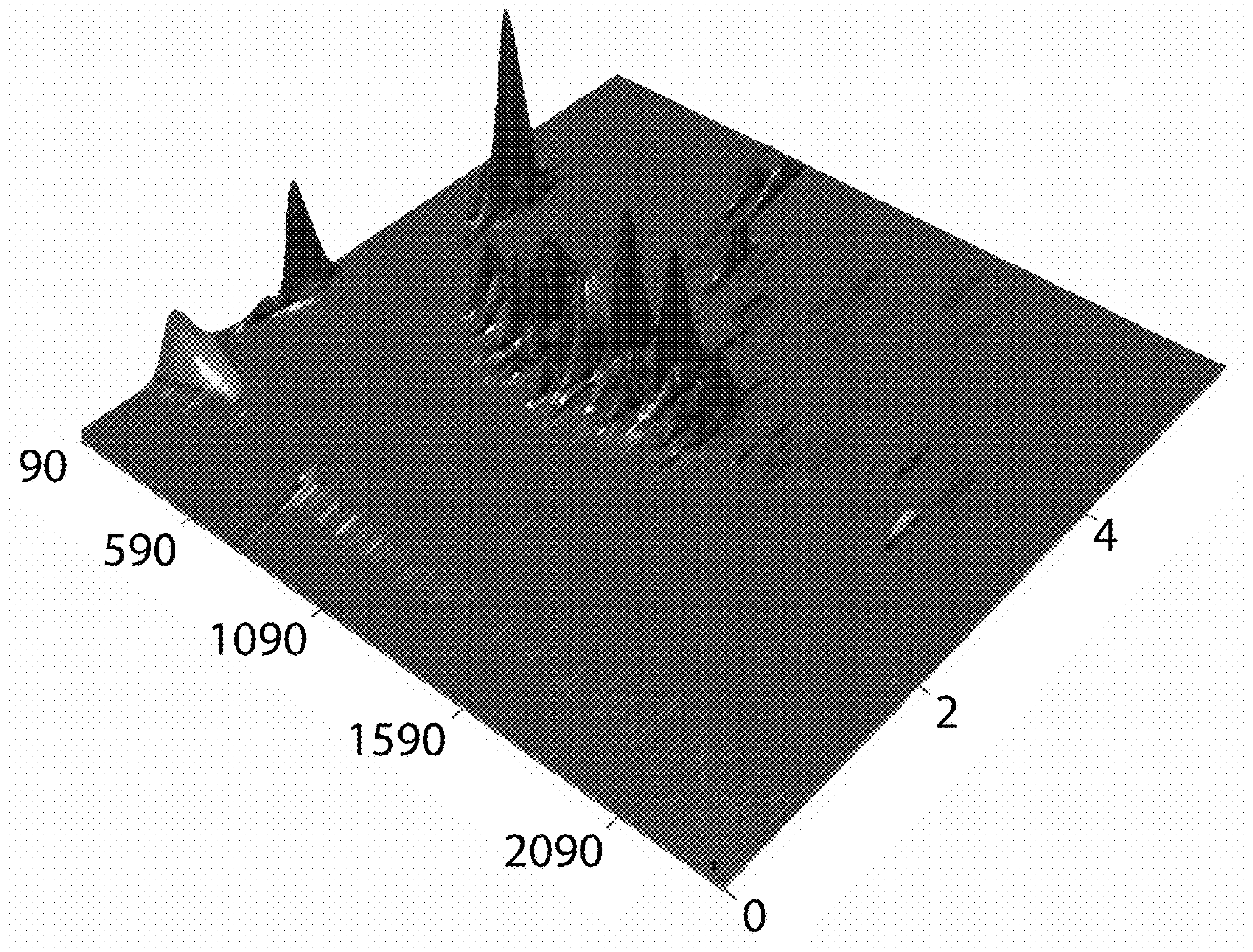


Figure 4C

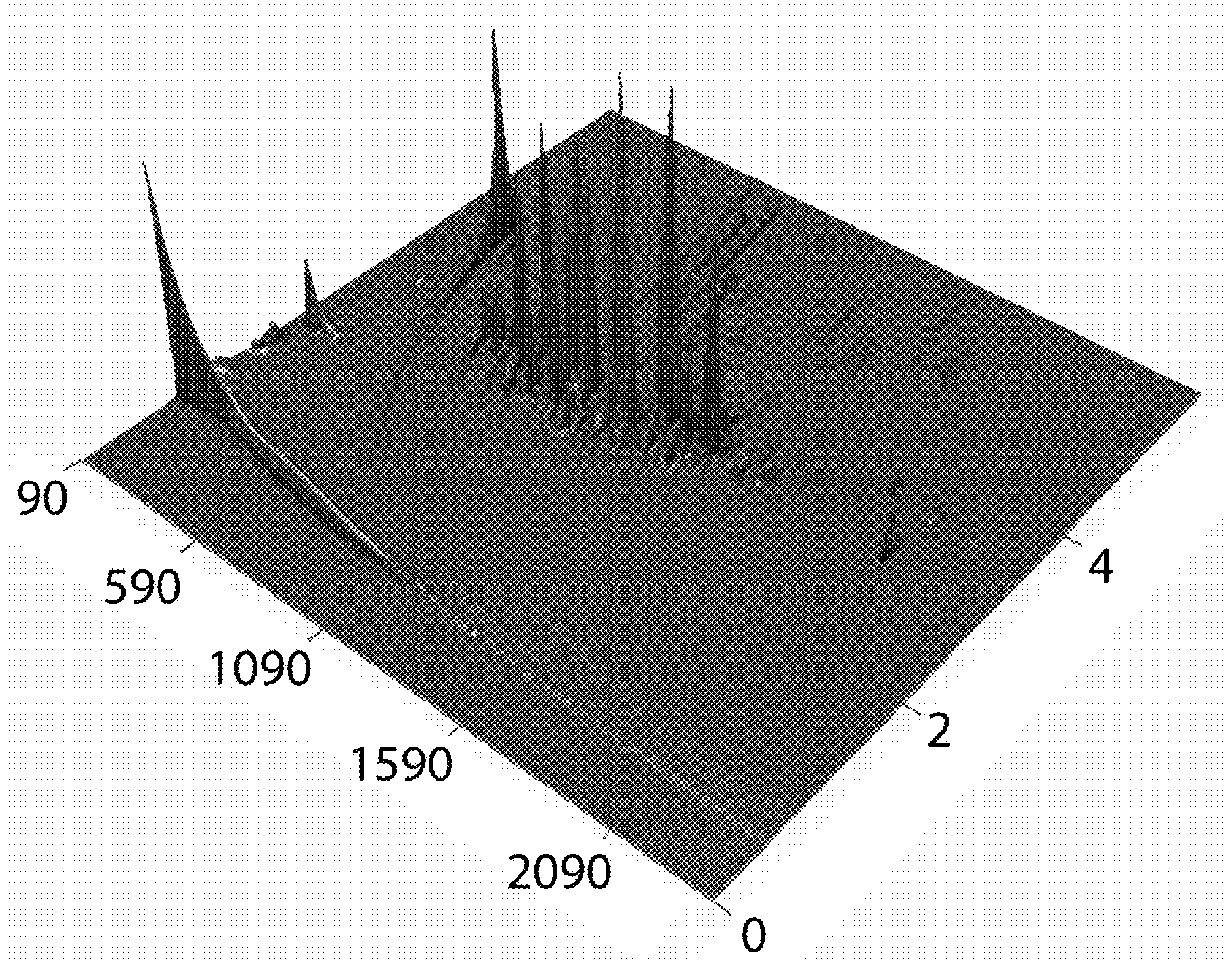


Figure 4D

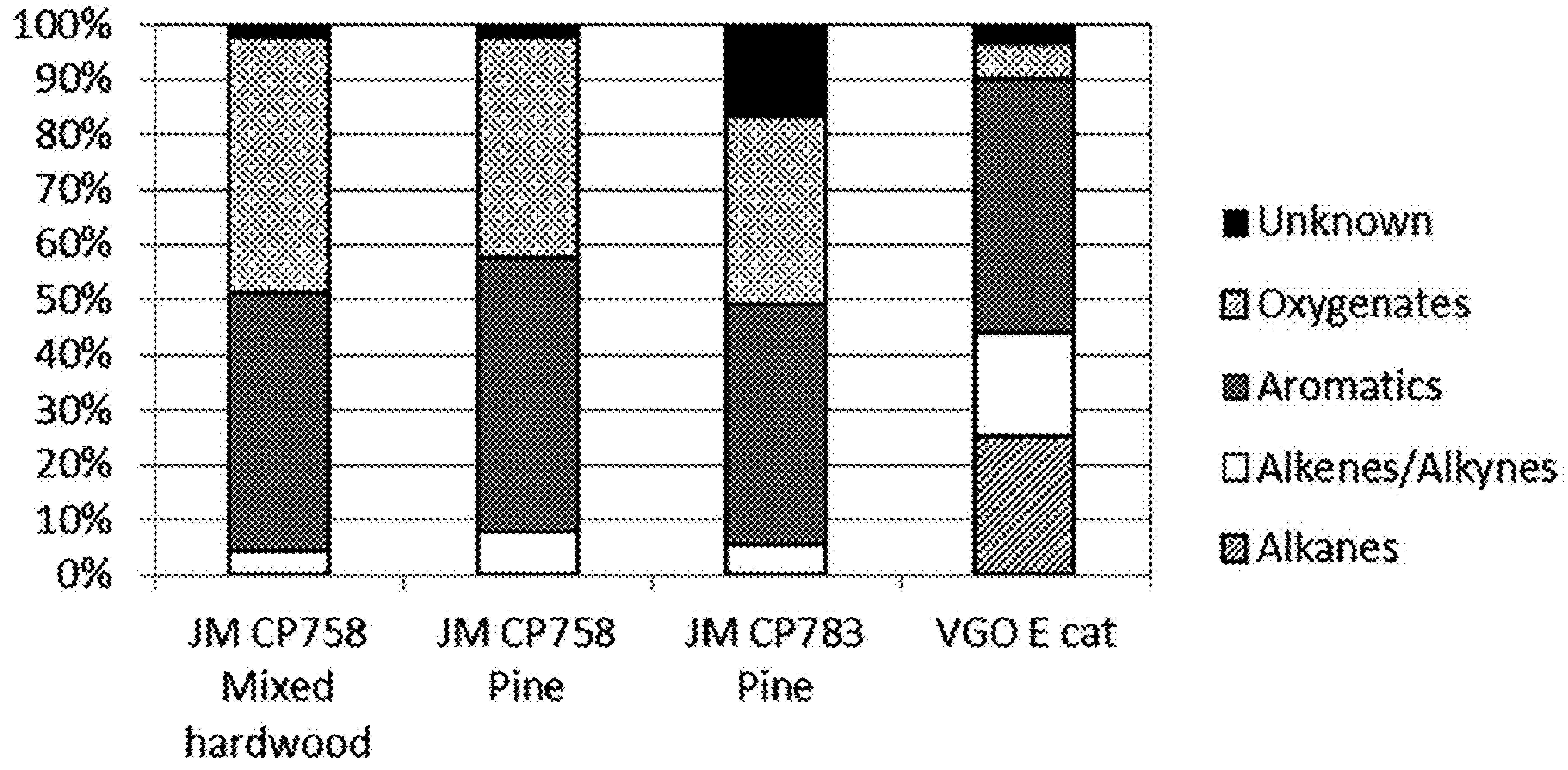

100%
90%
80%
70%
60%
50%
40%
30%
20%
10%
0%
JM CP758 Mixed hardwood
JM CP758 Pine
JM CP783 Pine
VGO E cat
■ Unknown
▨ Oxygenates
▩ Aromatics
☐ Alkenes/Alkynes
▨ Alkanes

Figure 5A

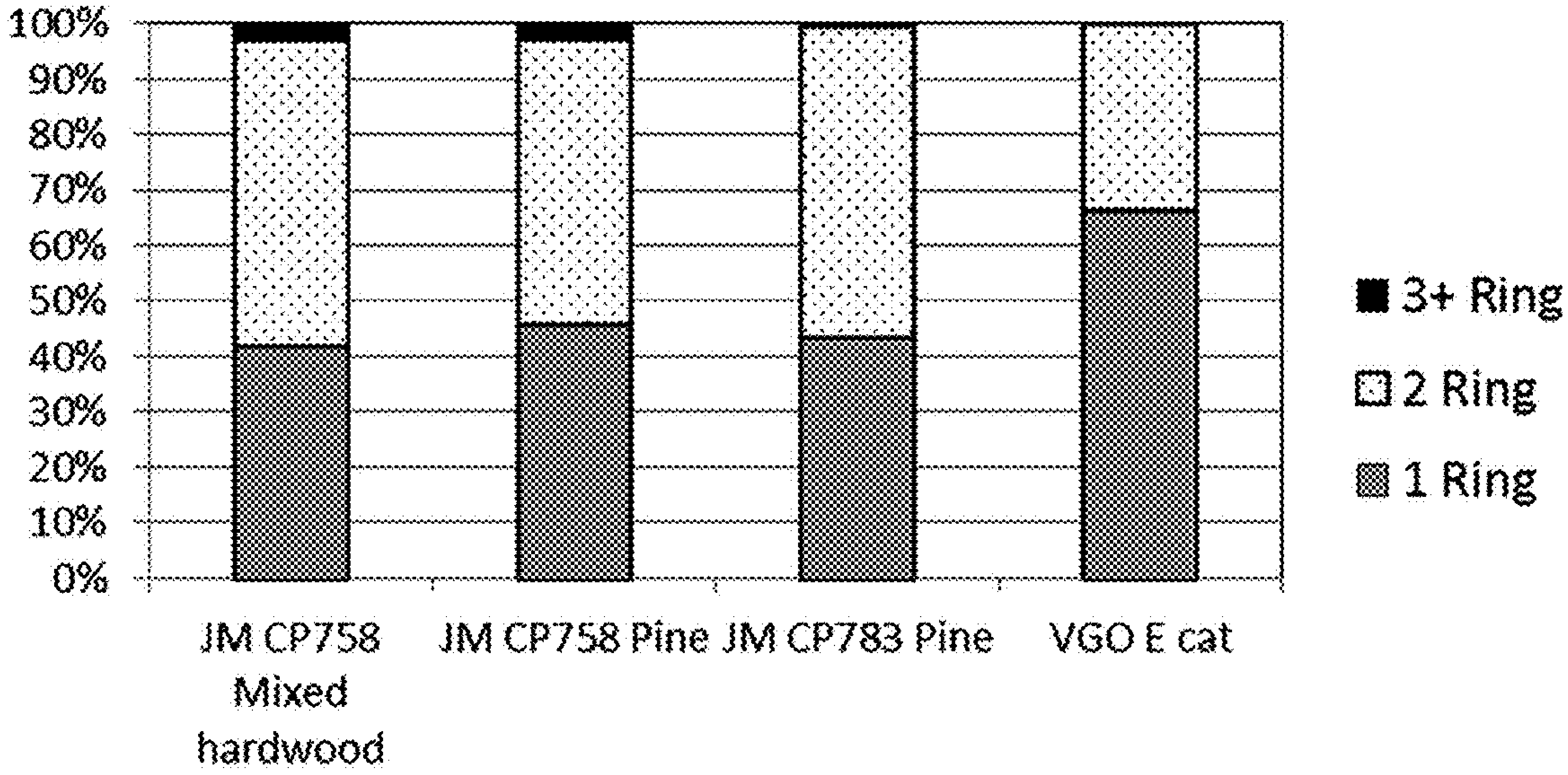

100%
90%
80%
70%
60%
50%
40%
30%
20%
10%
0%
JM CP758 Mixed hardwood
JM CP758 Pine
JM CP783 Pine
VGO E cat
■ 3+ Ring
▨ 2 Ring
▩ 1 Ring

Figure 5B

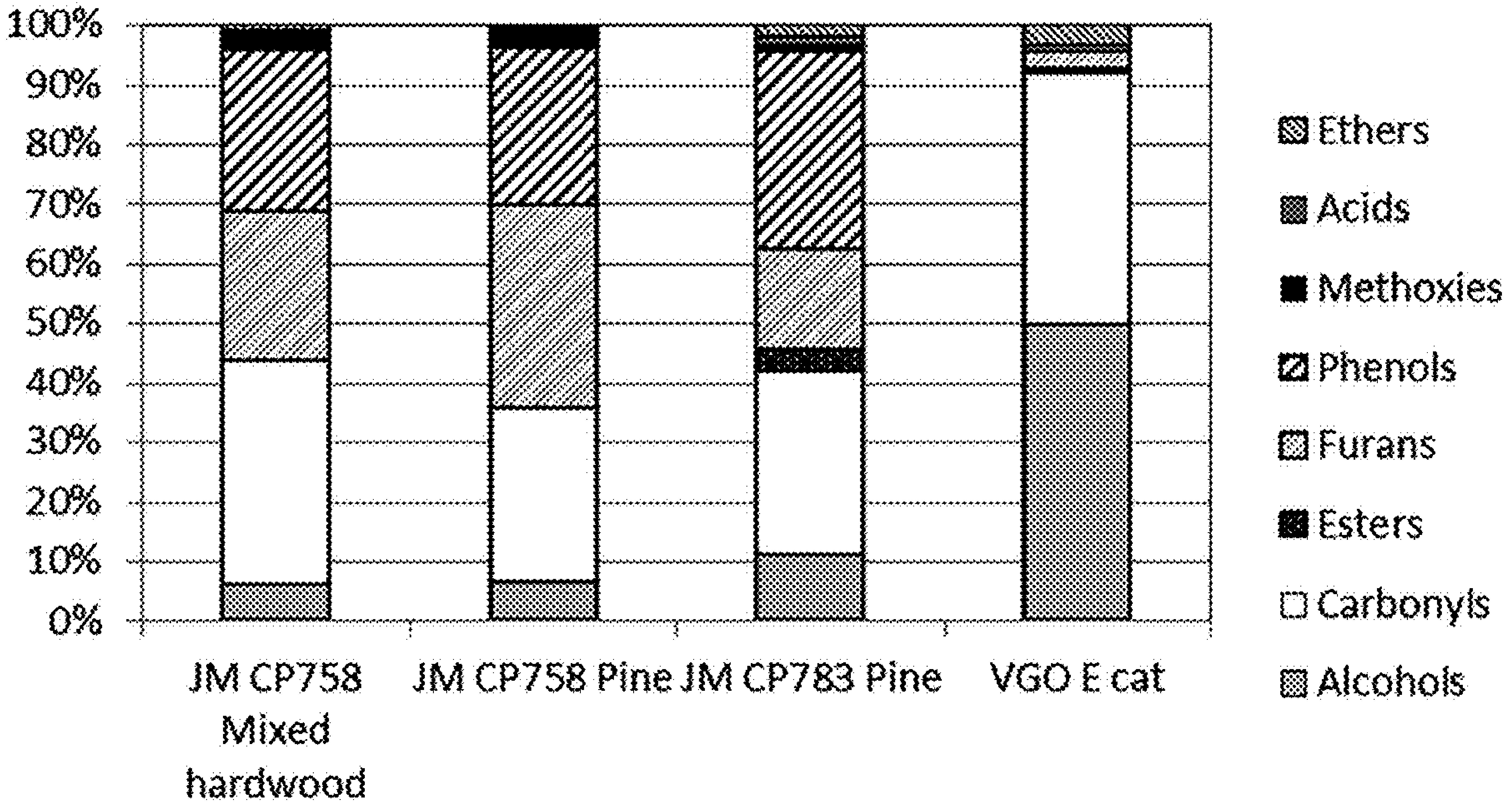

100%
90%
80%
70%
60%
50%
40%
30%
20%
10%
0%
JM CP758 Mixed hardwood
JM CP758 Pine
JM CP783 Pine
VGO E cat
Ethers
Acids
Methoxies
Phenols
Furans
Esters
Carbonyls
Alcohols

Figure 5C

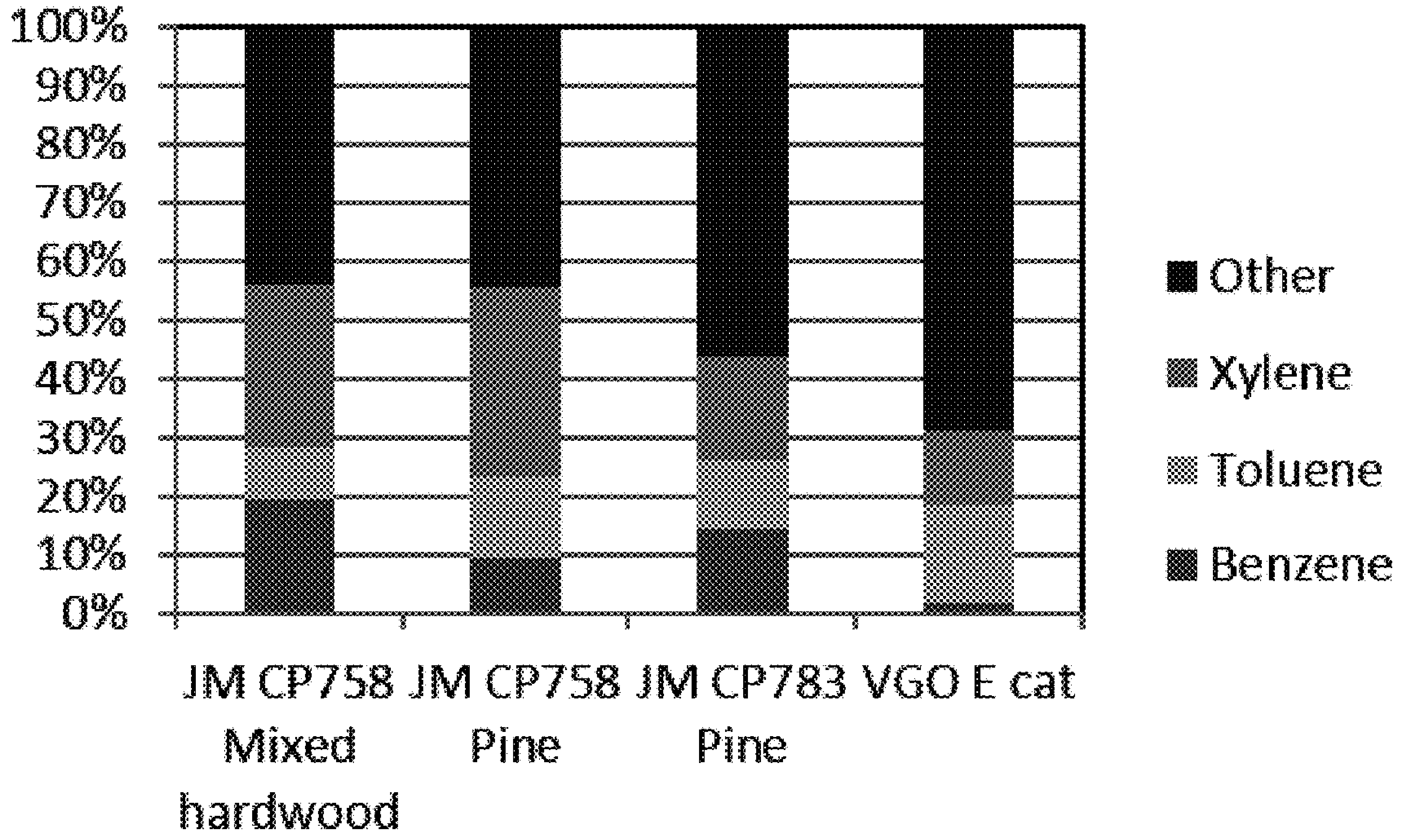

100%
90%
80%
70%
60%
50%
40%
30%
20%
10%
0%
JM CP758 Mixed hardwood
JM CP758 Pine
JM CP783 Pine
VGO E cat
Other
Xylene
Toluene
Benzene

Figure 5D

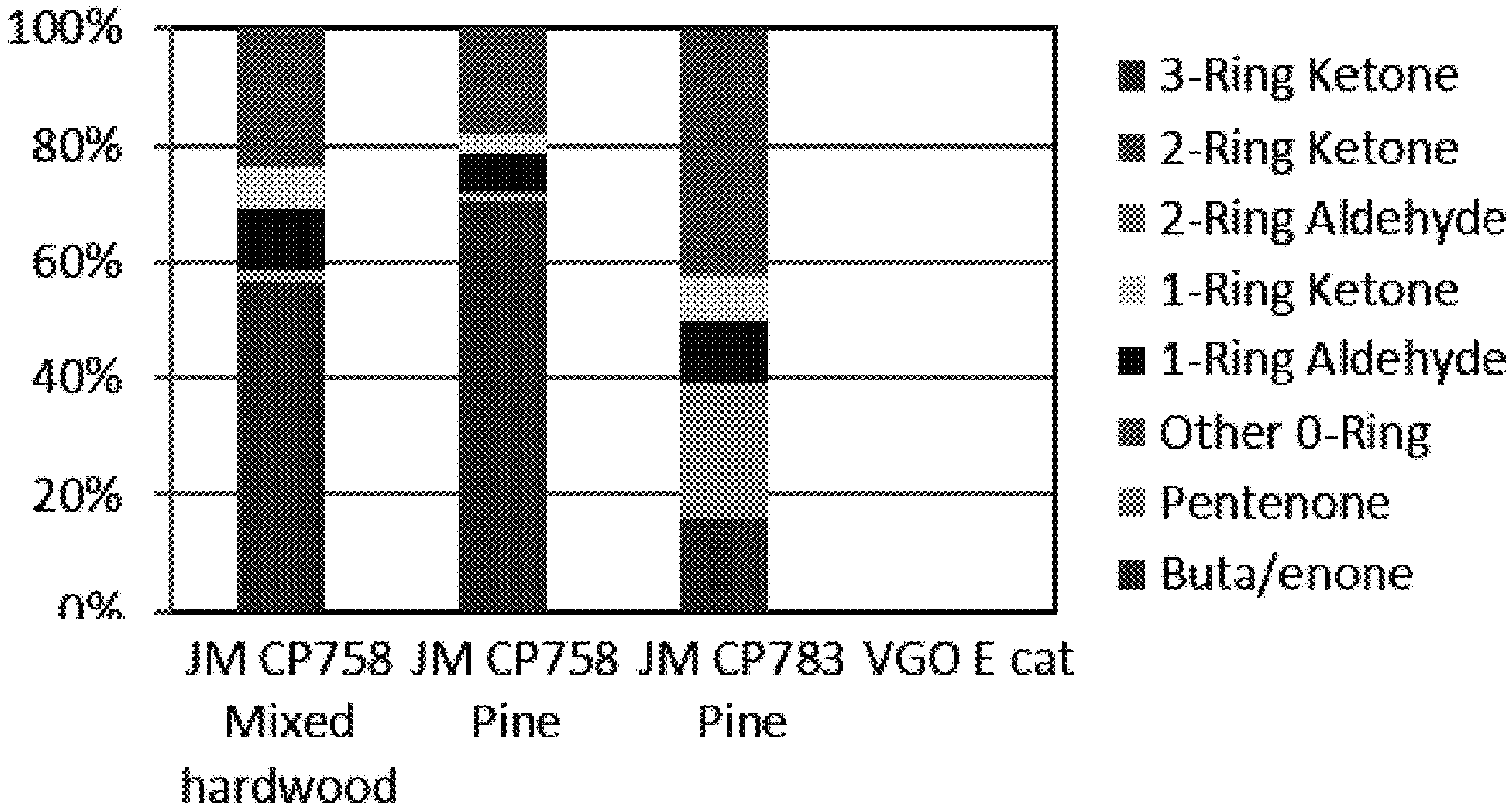

100%
80%
60%
40%
20%
0%
JM CP758 Mixed hardwood
JM CP758 Pine
JM CP783 Pine
VGO E cat
3-Ring Ketone
2-Ring Ketone
2-Ring Aldehyde
1-Ring Ketone
1-Ring Aldehyde
Other 0-Ring
Pentenone
Buta/enone

Figure 5E

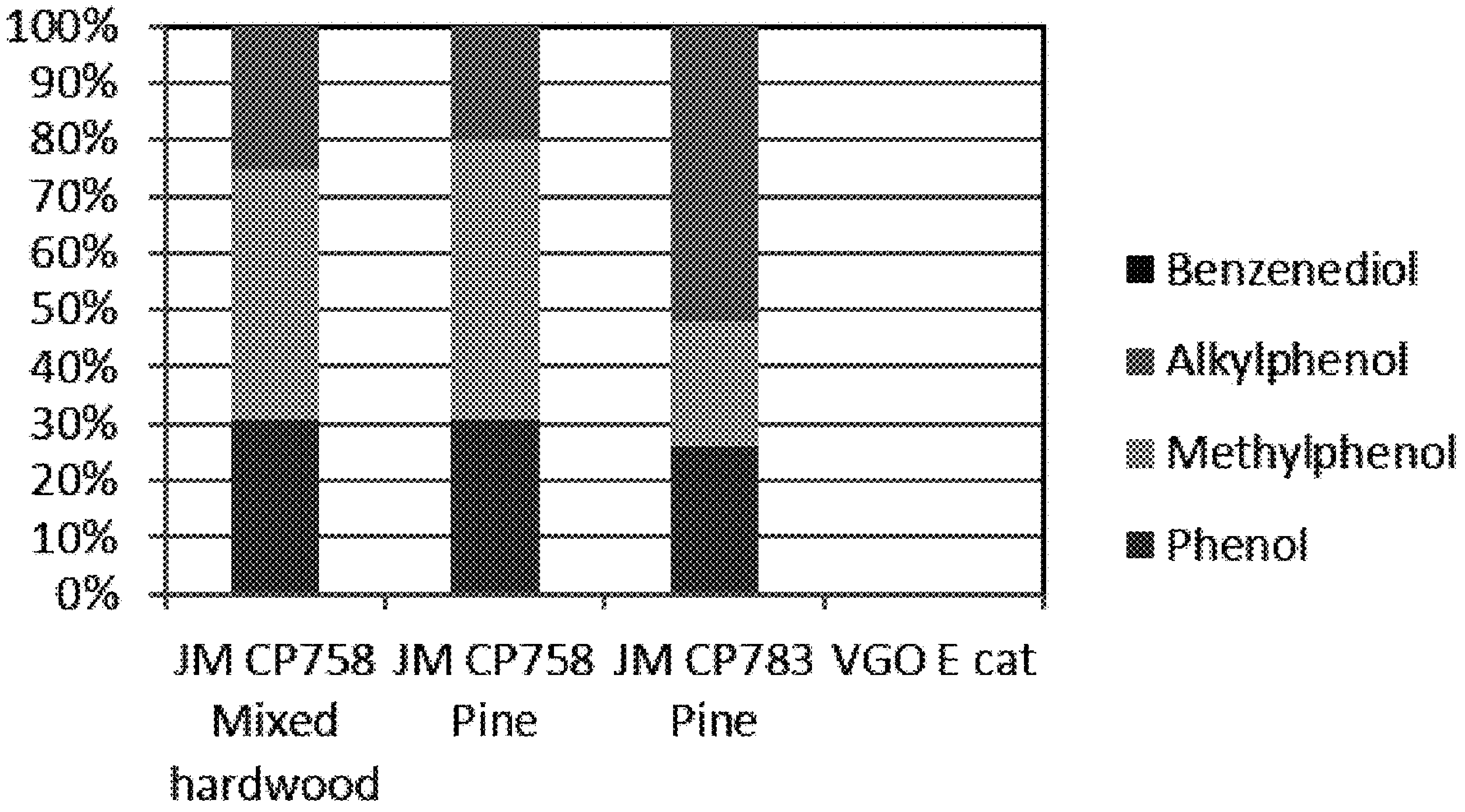

100%
90%
80%
70%
60%
50%
40%
30%
20%
10%
0%
JM CP758 Mixed hardwood
JM CP758 Pine
JM CP783 Pine
VGO E cat
Benzenediol
Alkylphenol
Methylphenol
Phenol

Figure 5F

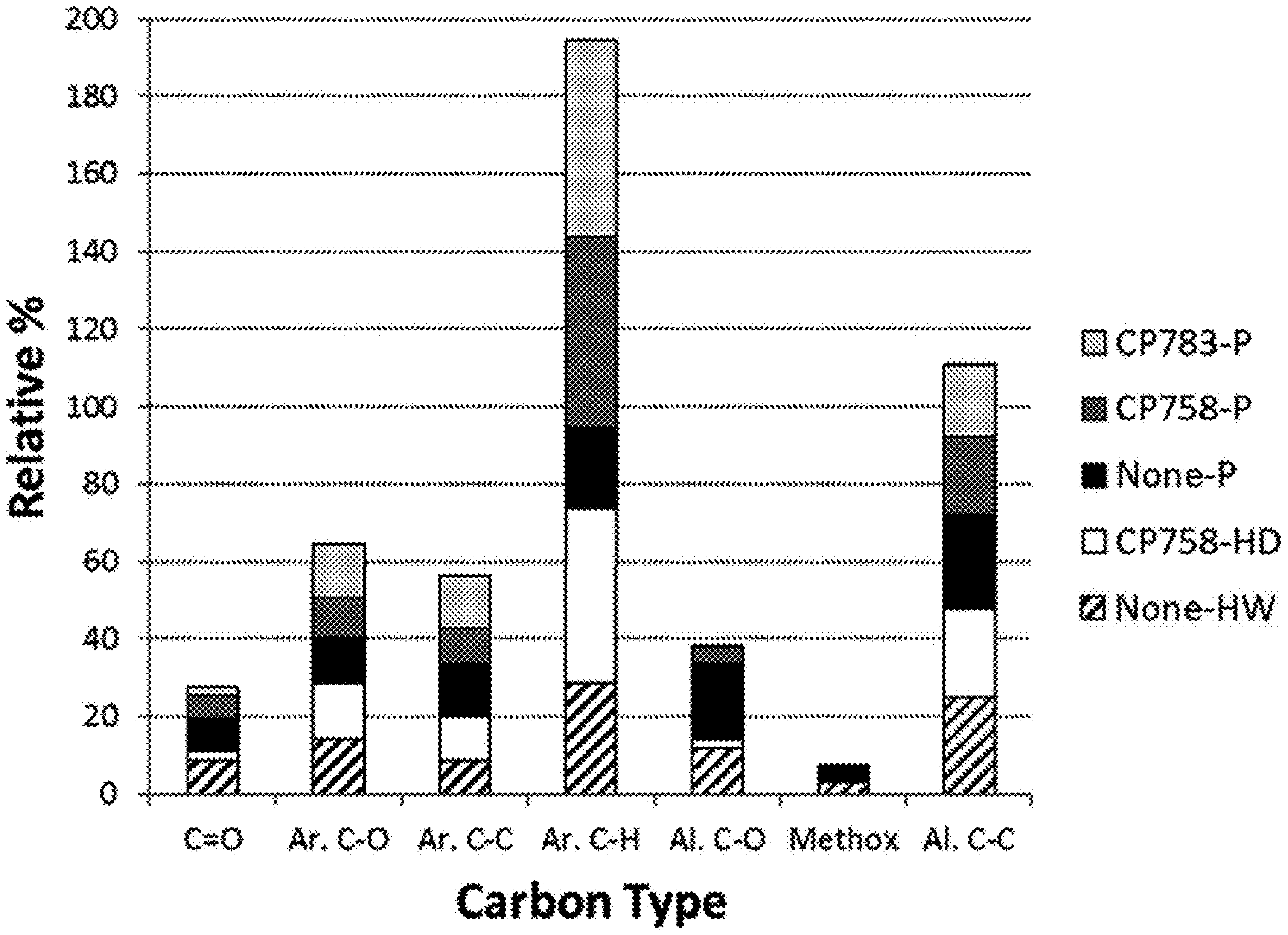

200
180
160
140
120
100
80
60
40
20
0
Relative %
C=O
Ar. C-O
Ar. C-C
Ar. C-H
Al. C-O
Methox
Al. C-C
Carbon Type
CP783-P
CP758-P
None-P
CP758-HD
None-HW

Figure 6

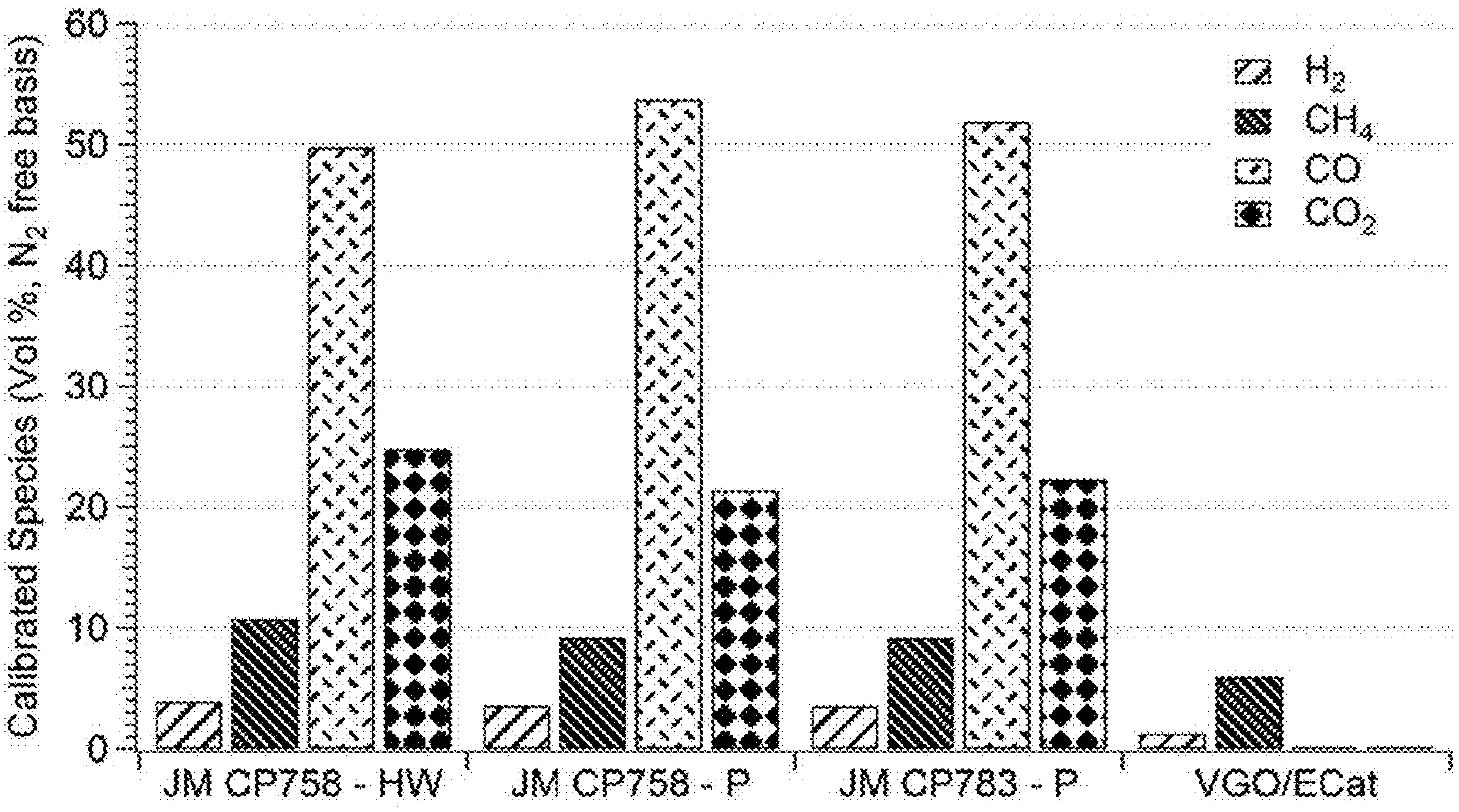

Calibrated Species (Vol %, N$_2$ free basis)
0
10
20
30
40
50
60
H$_2$
CH$_4$
CO
CO$_2$
JM CP758 - HW
JM CP758 - P
JM CP783 - P
VGO/ECat

Figure 7

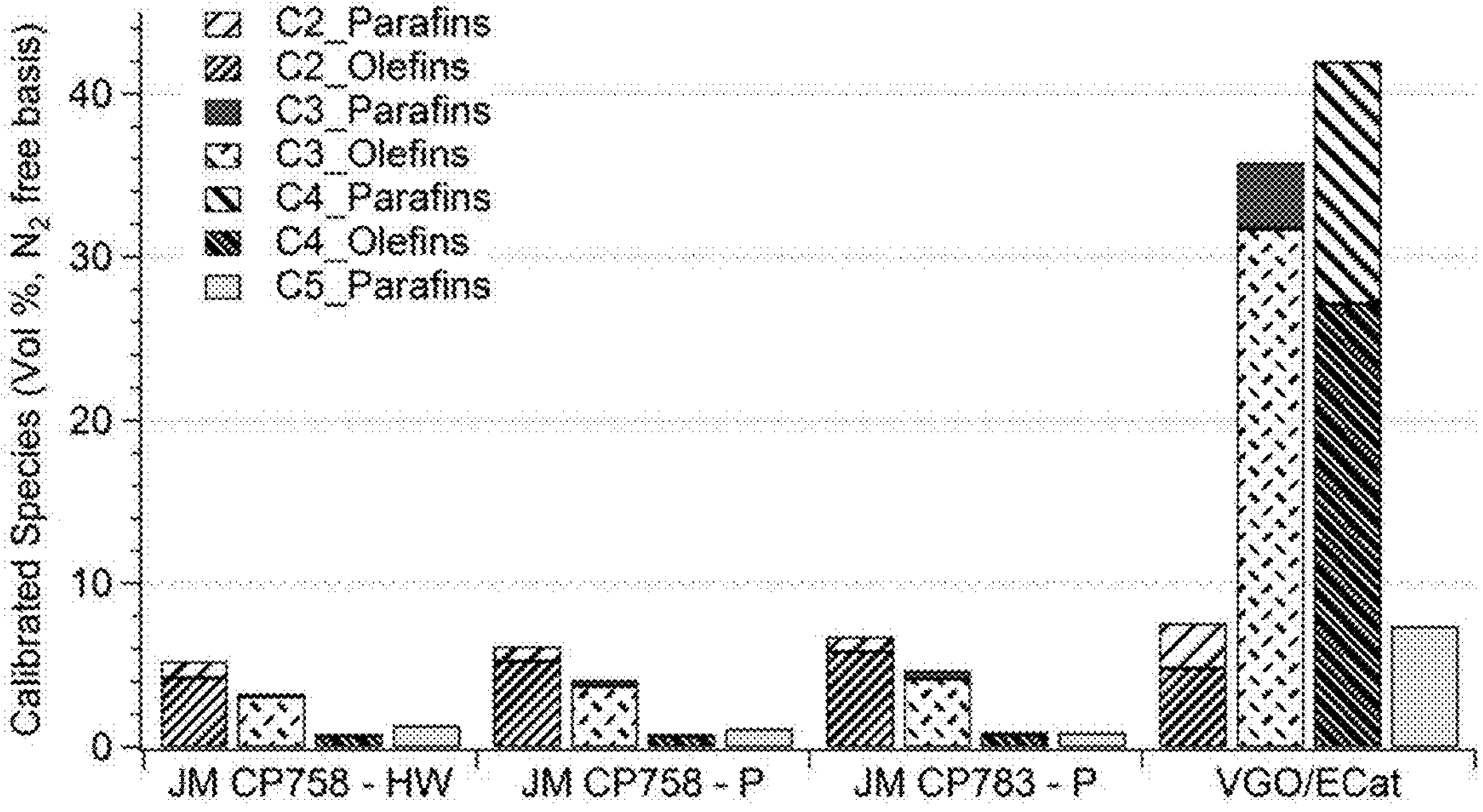

C2_Parafins
C2_Olefins
C3_Parafins
C3_Olefins
C4_Parafins
C4_Olefins
C5_Parafins
Calibrated Species (Vol %, N₂ free basis)
0
10
20
30
40
JM CP758 - HW
JM CP758 - P
JM CP783 - P
VGO/ECat

Figure 8

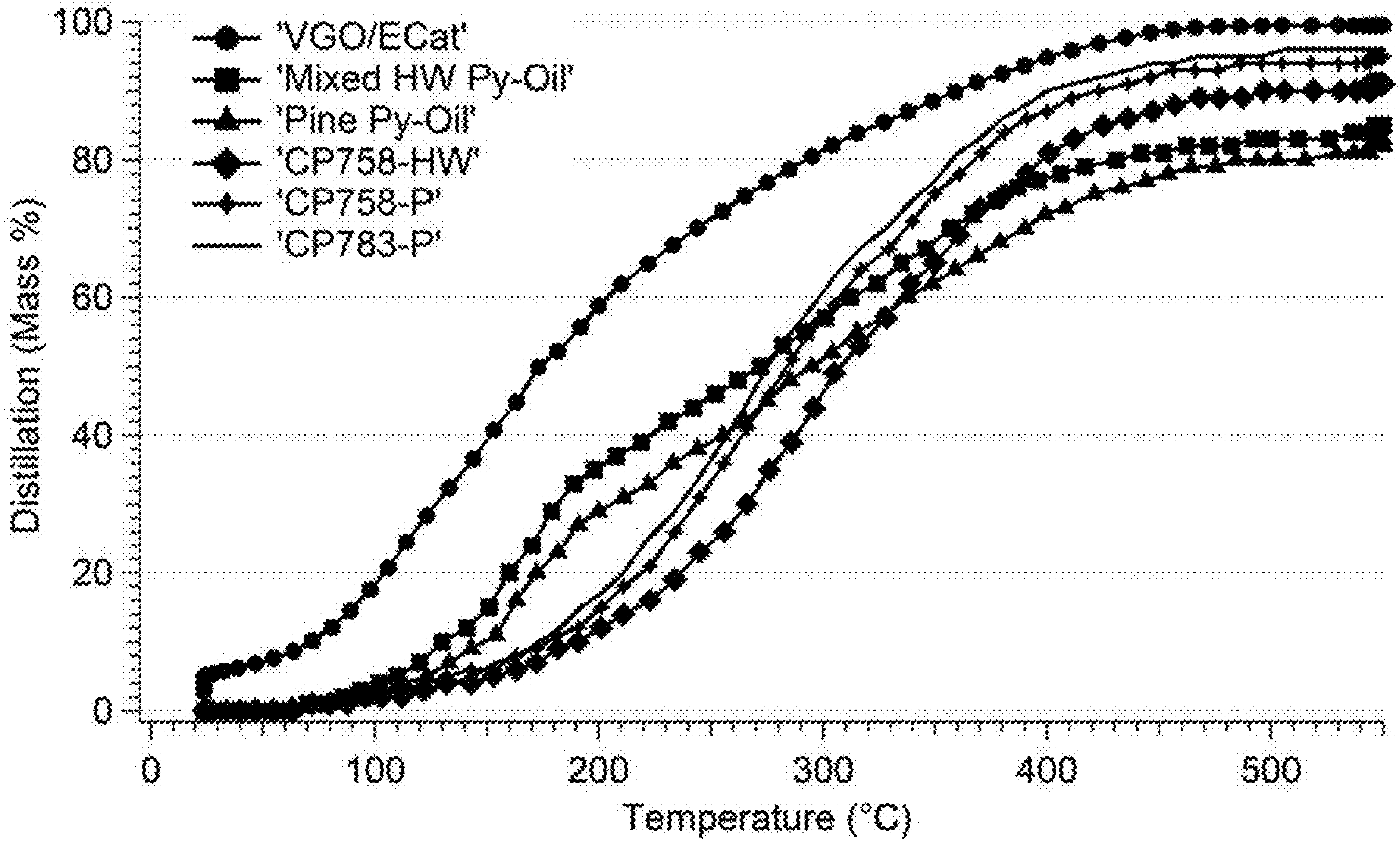

'VGO/ECat'
'Mixed HW Py-Oil'
'Pine Py-Oil'
'CP758-HW'
'CP758-P'
'CP783-P'
Distillation (Mass %)
0
20
40
60
80
100
Temperature (°C)
0
100
200
300
400
500

Figure 9

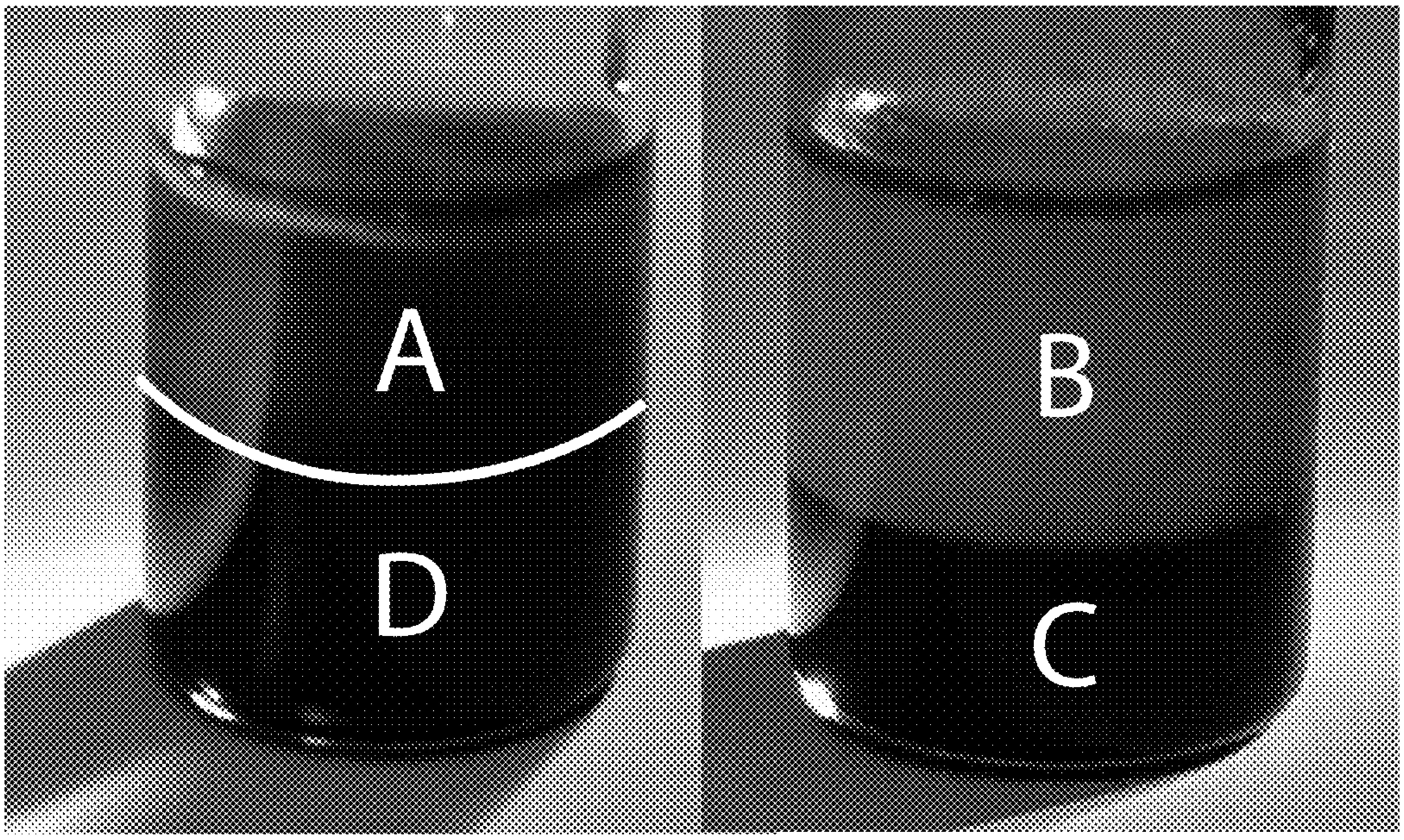


Figure 10

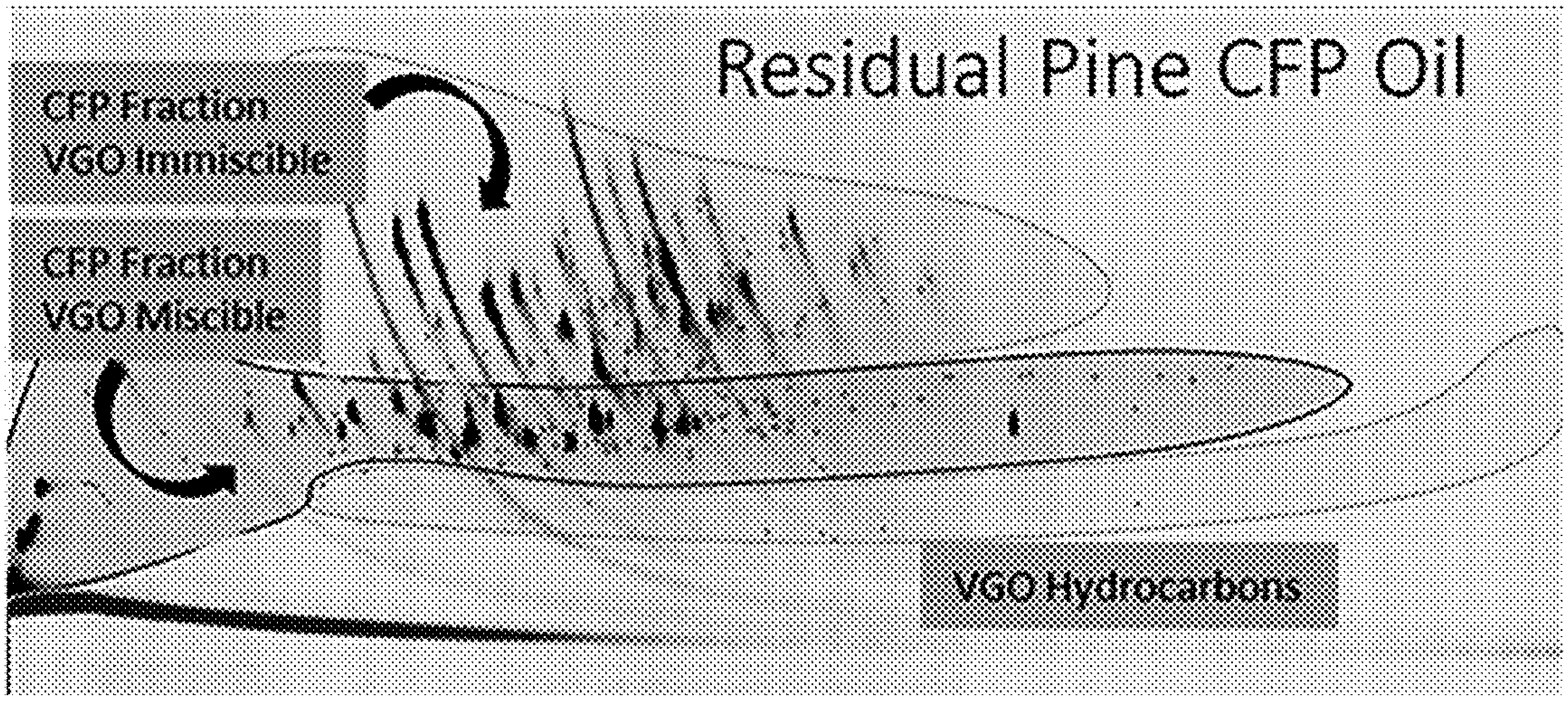

Residual Pine CFP Oil
CFP Fraction
VGO Immiscible
CFP Fraction
VGO Miscible
VGO Hydrocarbons

Figure 11A

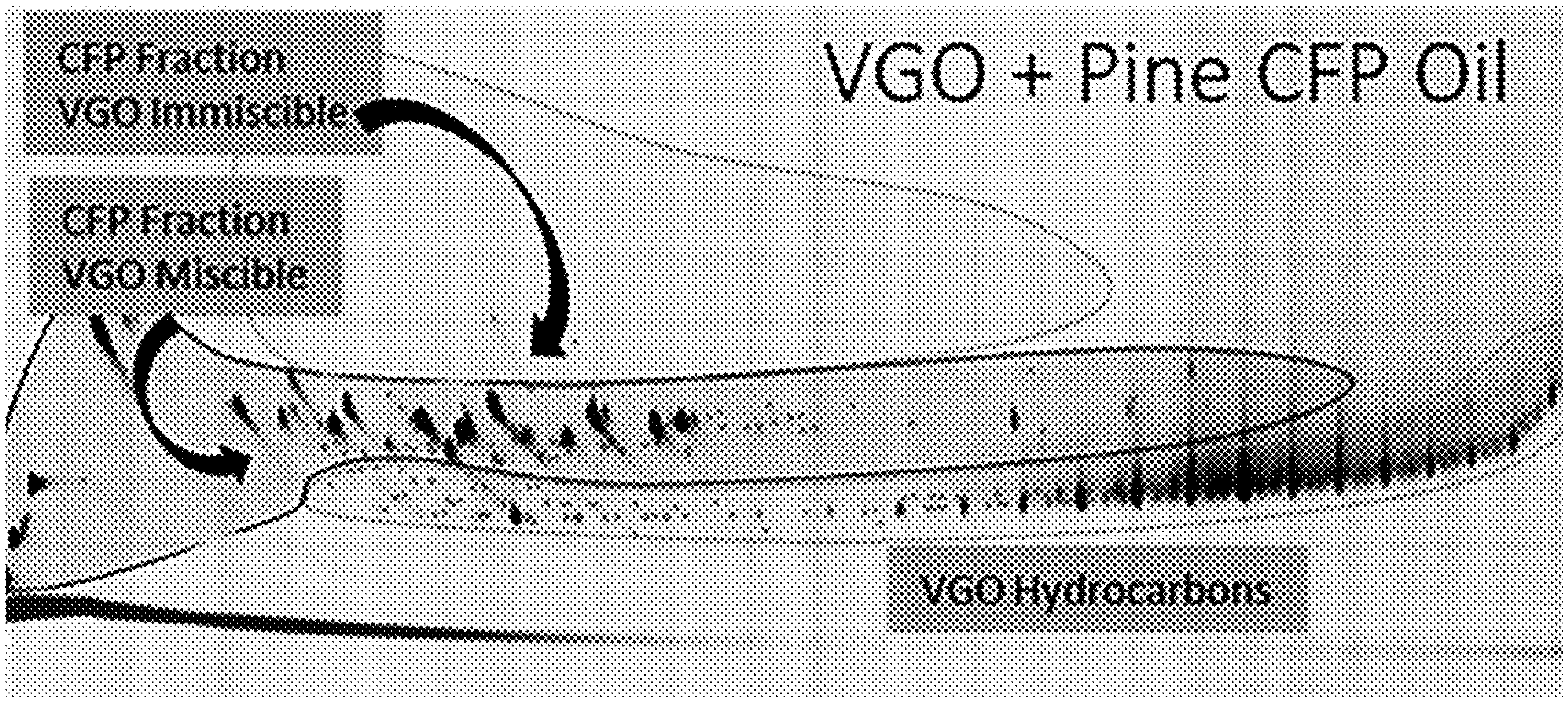

CFP Fraction
VGO Immiscible
CFP Fraction
VGO Miscible
VGO + Pine CFP Oil
VGO Hydrocarbons

Figure 11B

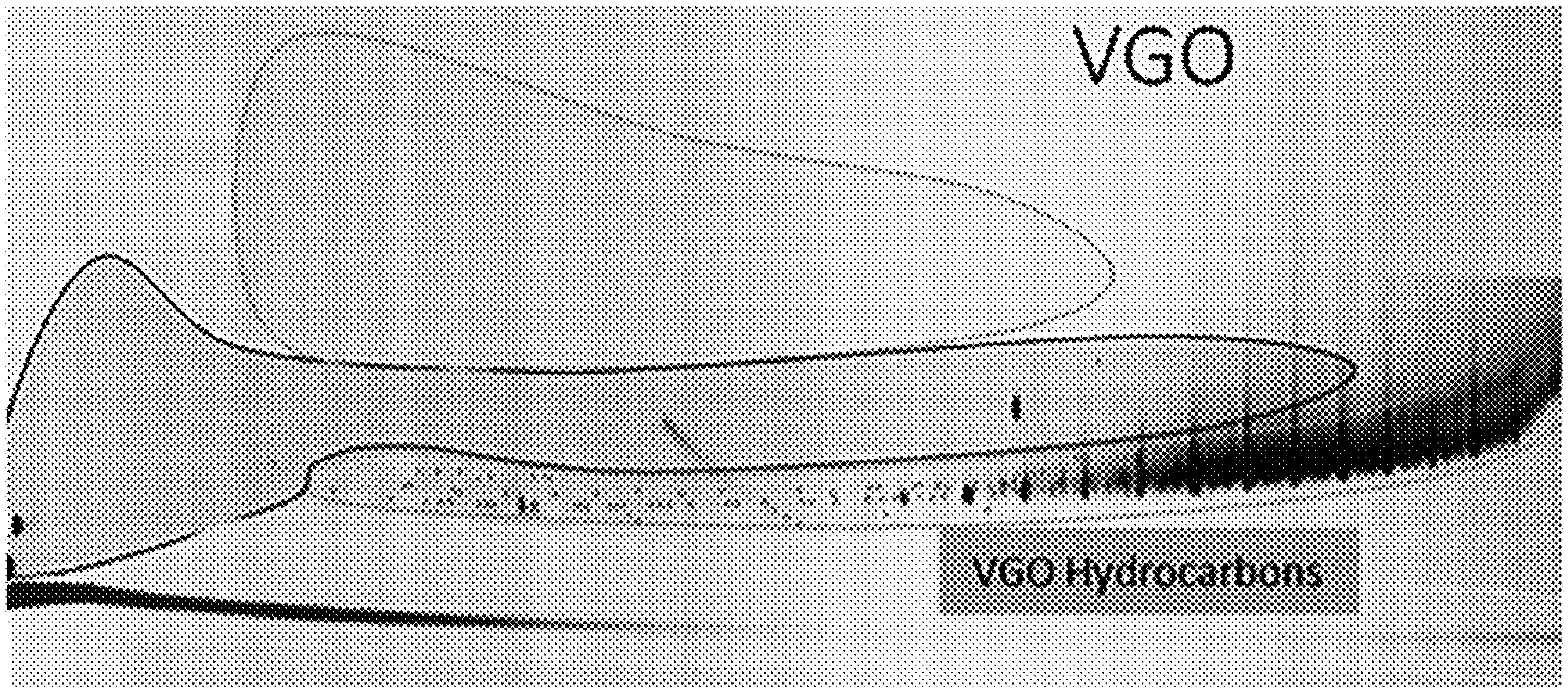


Figure 11C

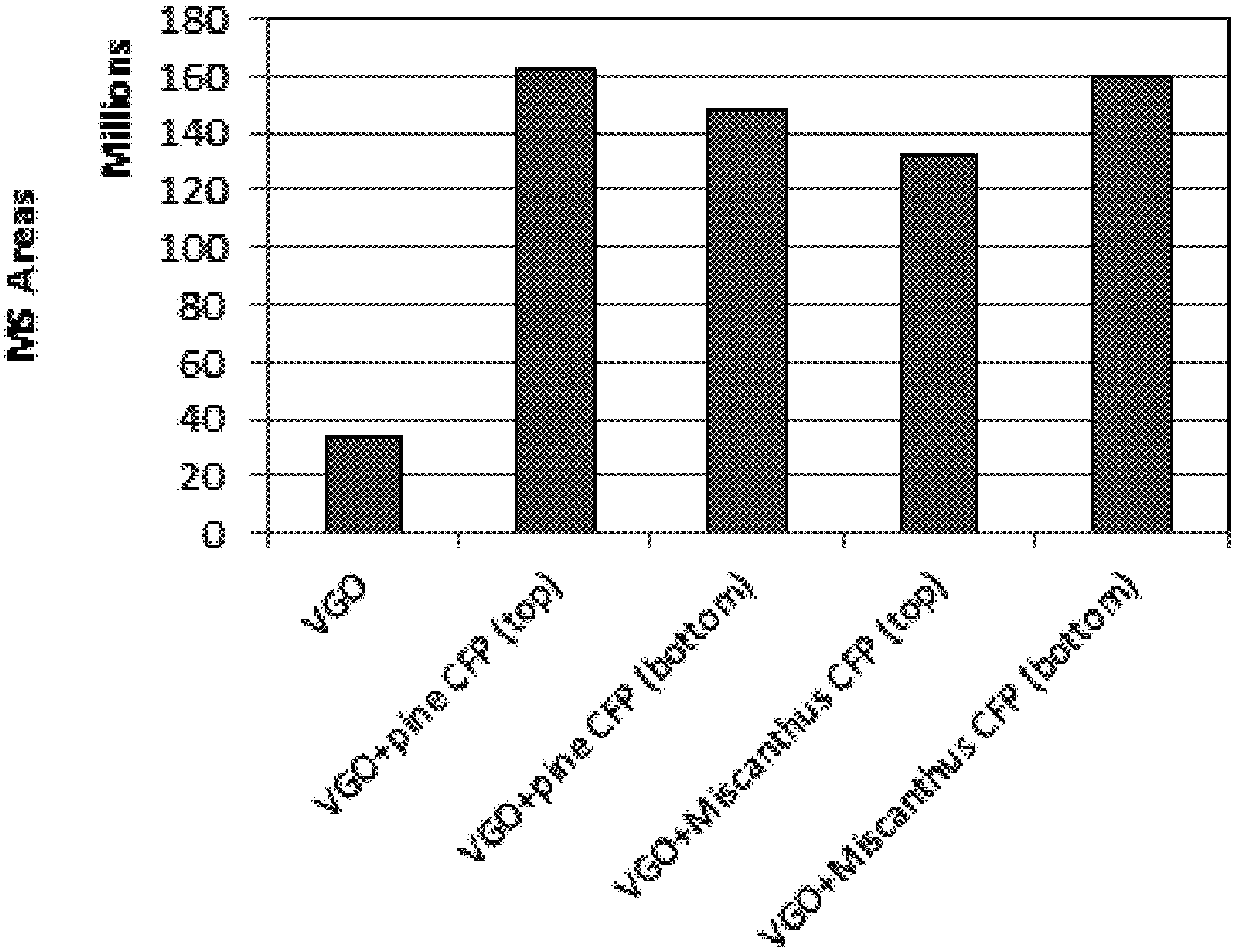

MS Areas
Millions
180
160
140
120
100
80
60
40
20
0
VGO
VGO+pine CFP (top)
VGO+pine CFP (bottom)
VGO+Miscanthus CFP (top)
VGO+Miscanthus CFP (bottom)

Figure 12

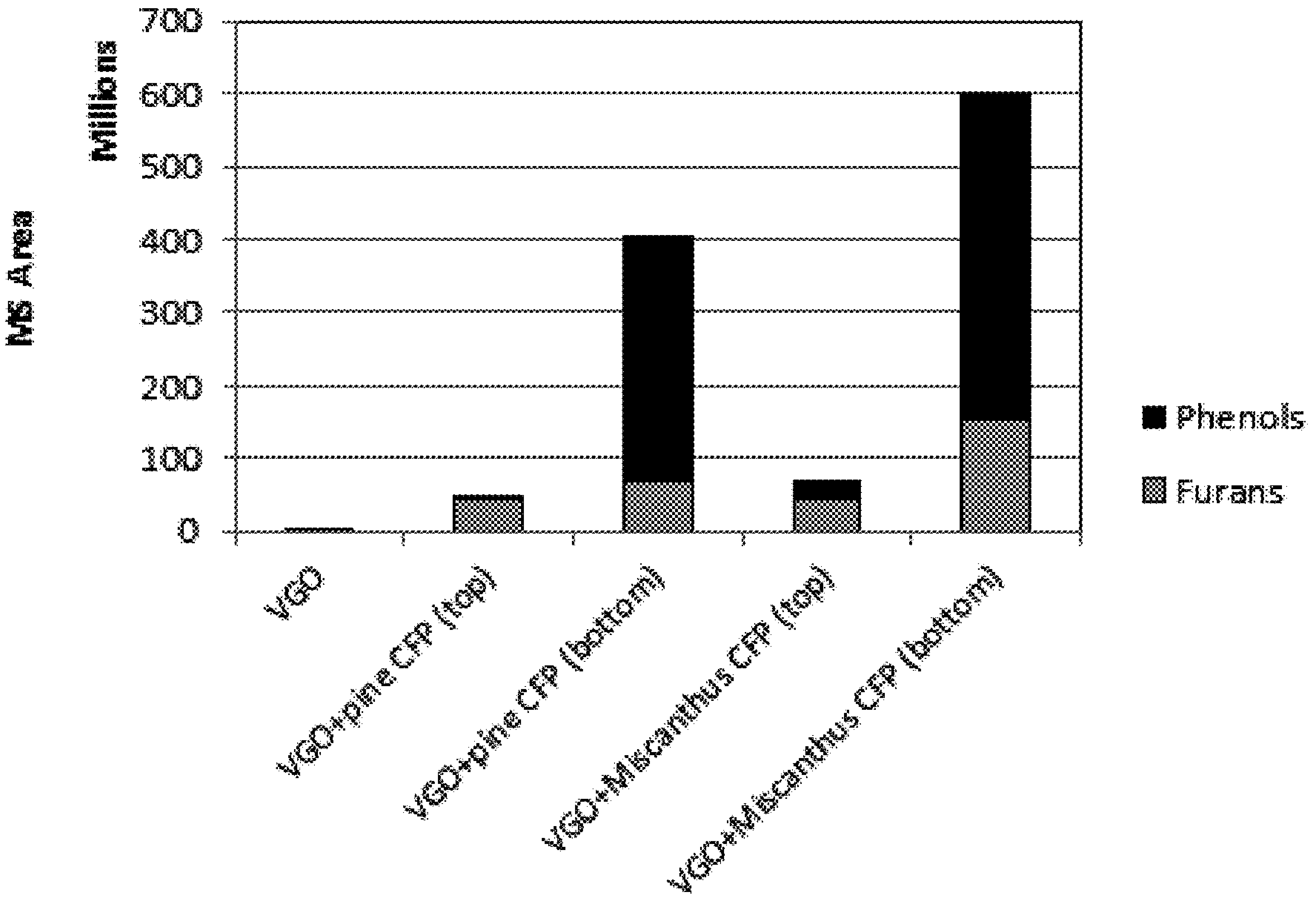

MS Area
Millions
700
600
500
400
300
200
100
0
Phenols
Furans
VGO
VGO+pine CFP (top)
VGO+pine CFP (bottom)
VGO+Miscanthus CFP (top)
VGO+Miscanthus CFP (bottom)

Figure 13

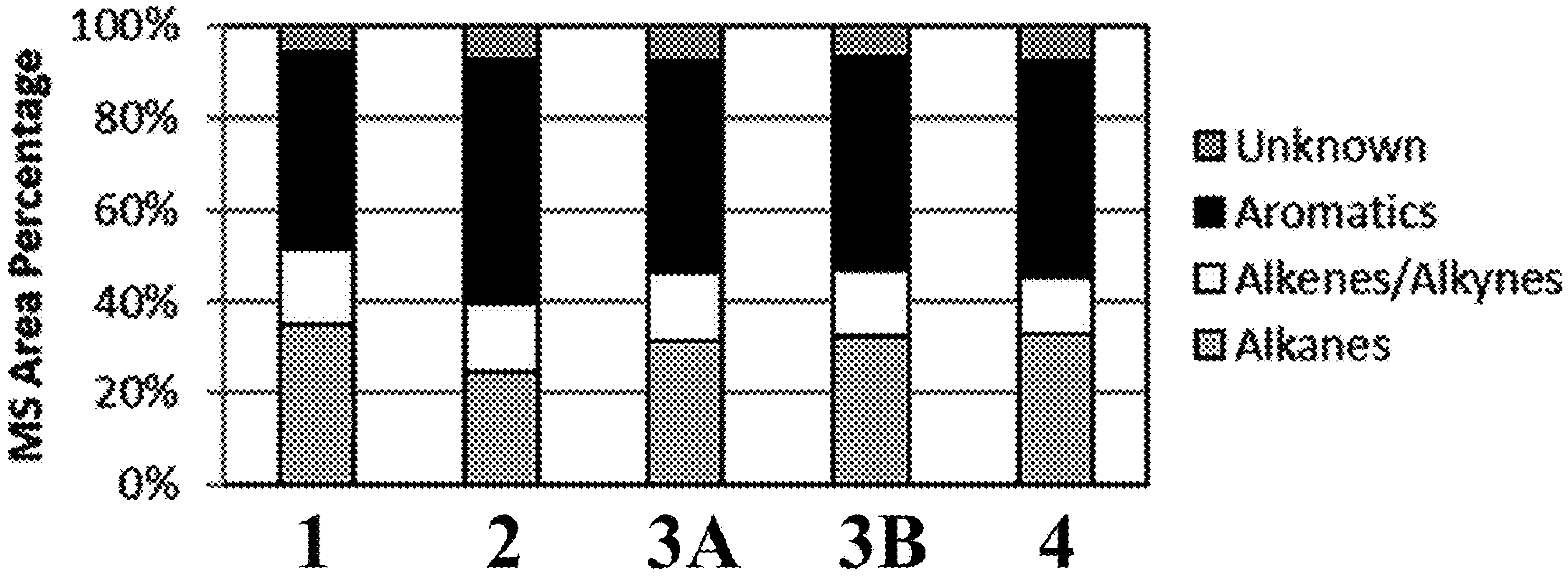

100%
80%
60%
40%
20%
0%
MS Area Percentage
Unknown
Aromatics
Alkenes/Alkynes
Alkanes
1
2
3A
3B
4

Figure 14A

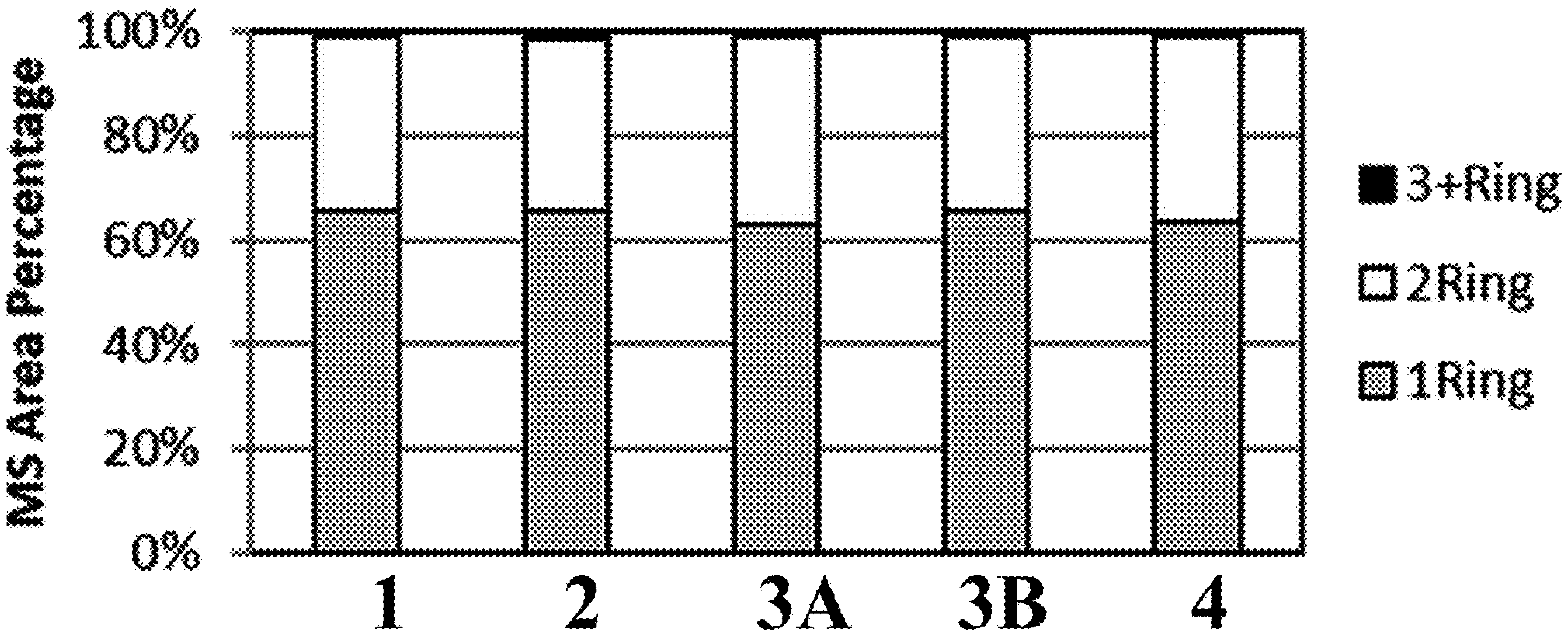

100%
80%
60%
40%
20%
0%
MS Area Percentage
■ 3+Ring
☐ 2Ring
▨ 1Ring
1
2
3A
3B
4

Figure 14B

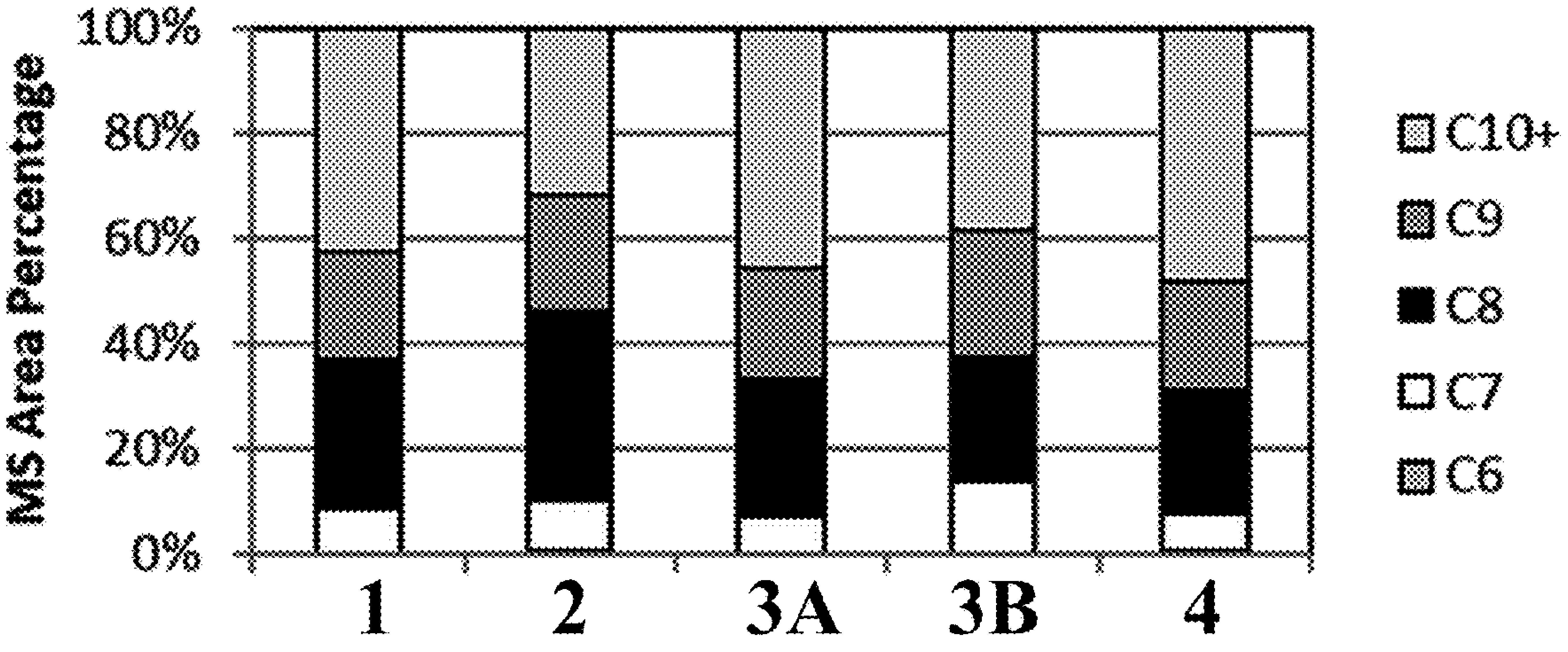


Figure 14C

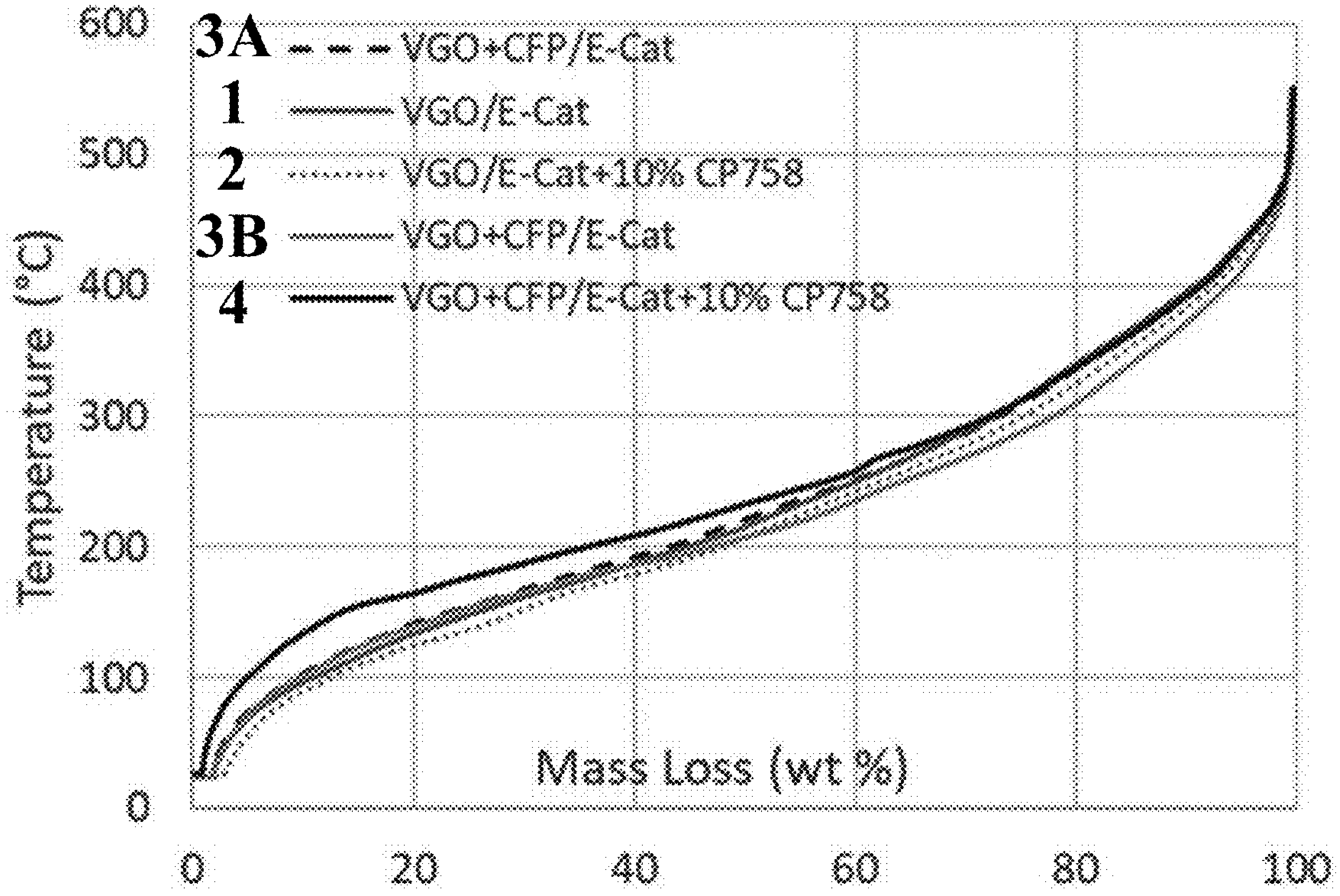
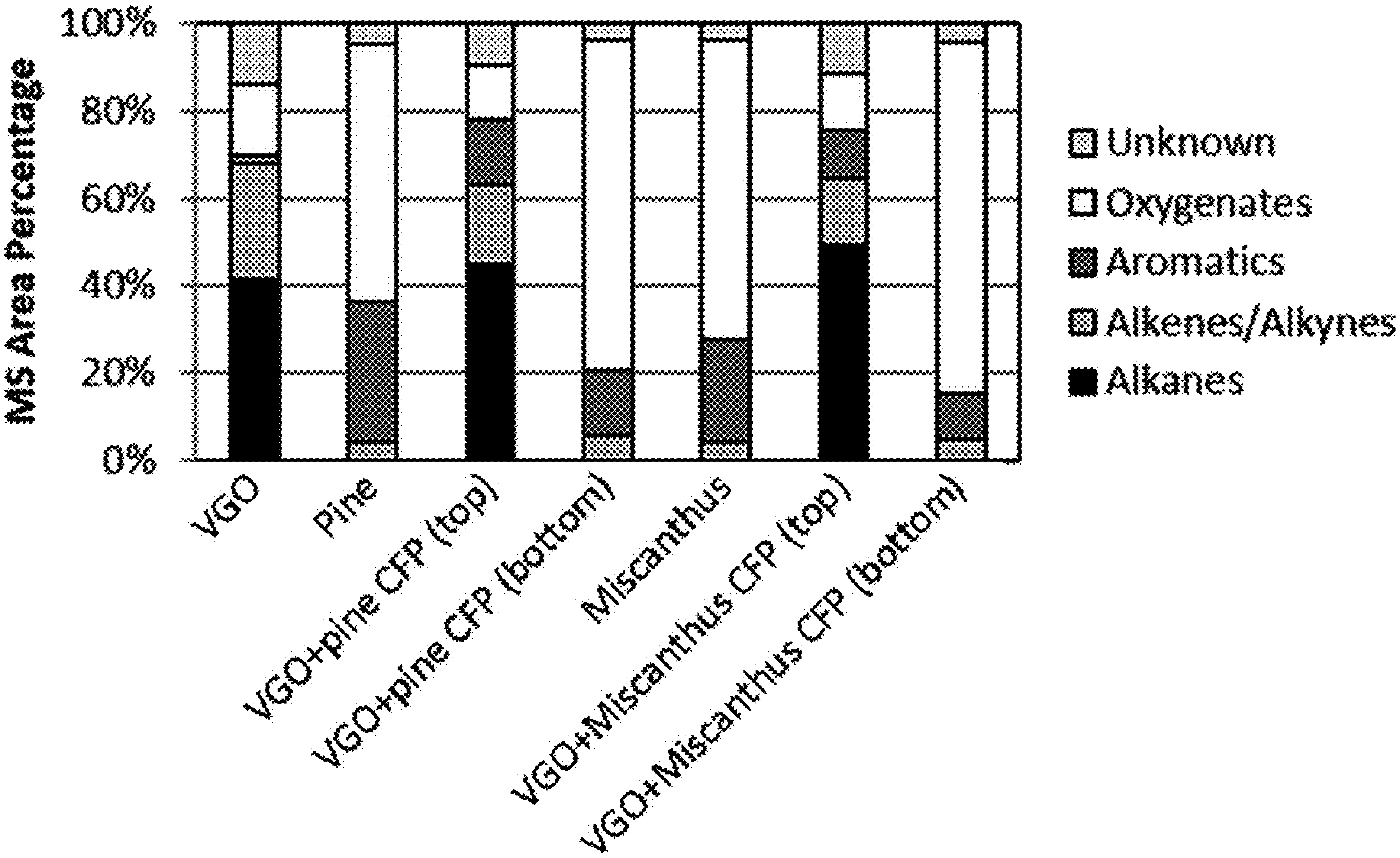

3A VGO+CFP/E-Cat
1 VGO/E-Cat
2 VGO/E-Cat+10% CP758
3B VGO+CFP/E-Cat
4 VGO+CFP/E-Cat+10% CP758
Temperature (°C)
600
500
400
300
200
100
0
Mass Loss (wt %)
0
20
40
60
80
100

Figure 15



MS Area Percentage
100%
80%
60%
40%
20%
0%
VGO
Pine
VGO+pine CFP (top)
VGO+pine CFP (bottom)
Miscanthus
VGO+Miscanthus CFP (top)
VGO+Miscanthus CFP (bottom)
▨ Unknown
☐ Oxygenates
▨ Aromatics
▨ Alkenes/Alkynes
■ Alkanes

Figure 16A

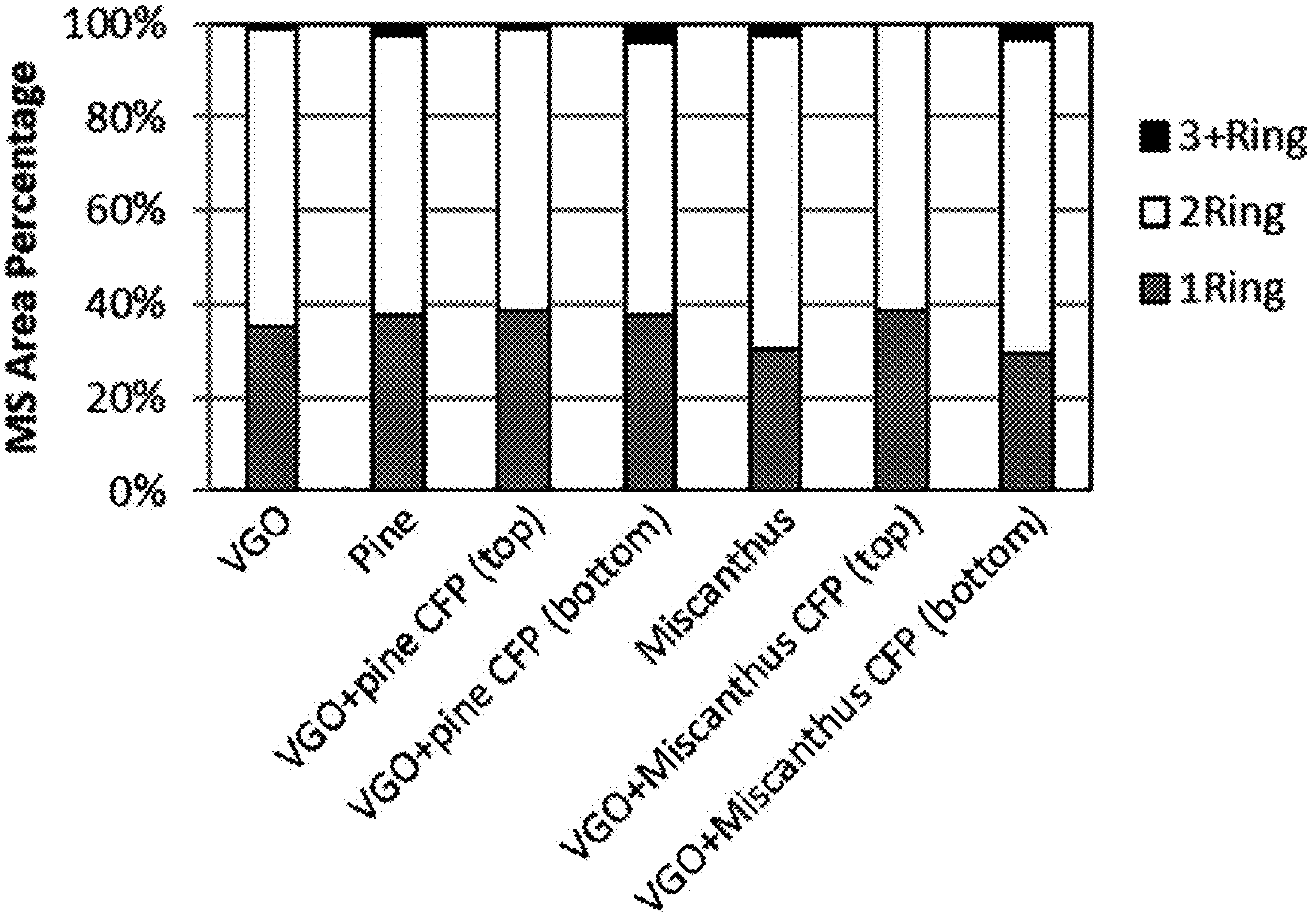

100%
80%
60%
40%
20%
0%
MS Area Percentage
■ 3+Ring
□ 2Ring
▨ 1Ring
VGO
Pine
VGO+pine CFP (top)
VGO+pine CFP (bottom)
Miscanthus
VGO+Miscanthus CFP (top)
VGO+Miscanthus CFP (bottom)

Figure 16B

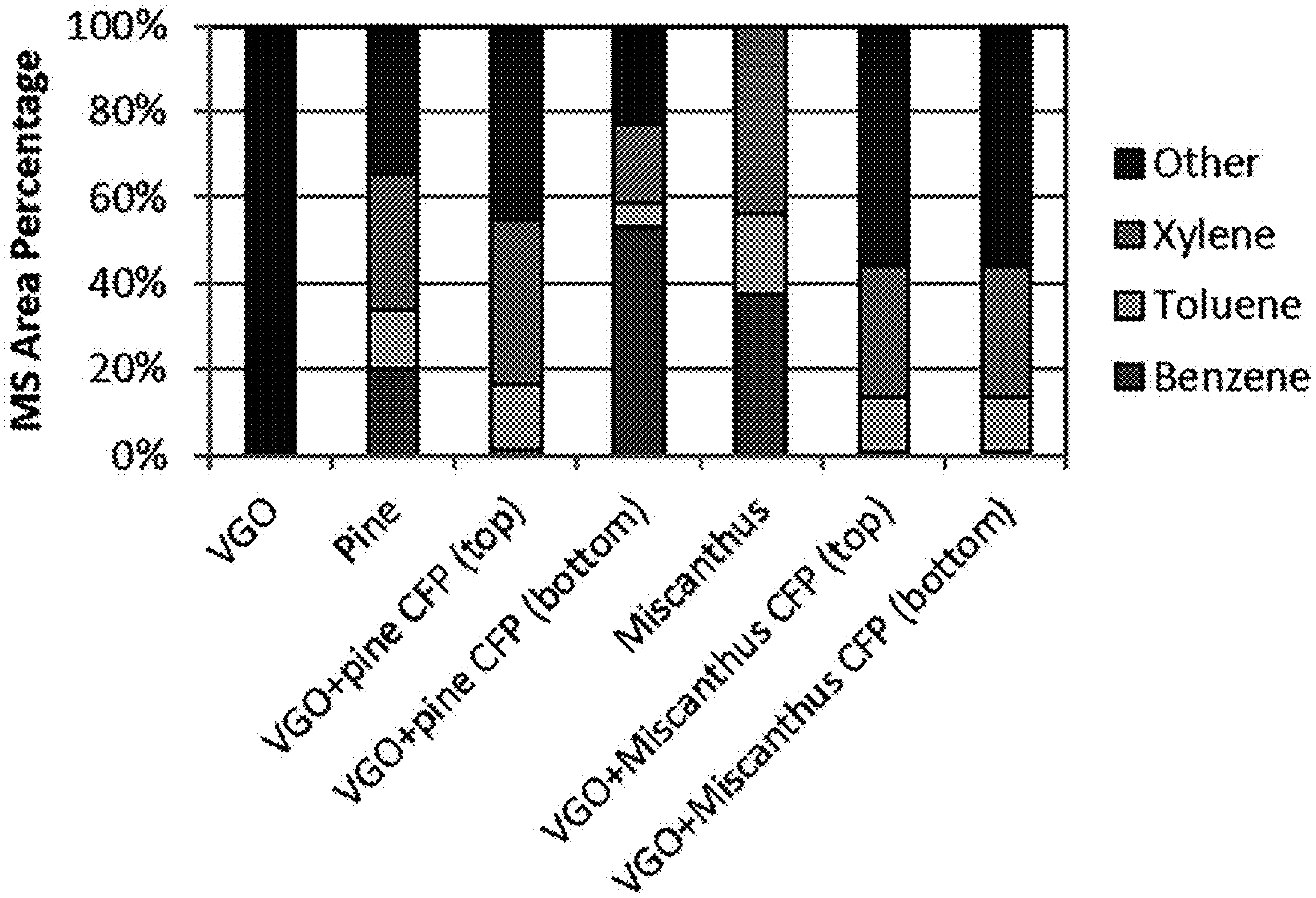

100%
80%
60%
40%
20%
0%
MS Area Percentage
VGO
Pine
VGO+pine CFP (top)
VGO+pine CFP (bottom)
Miscanthus
VGO+Miscanthus CFP (top)
VGO+Miscanthus CFP (bottom)
Other
Xylene
Toluene
Benzene

Figure 16C

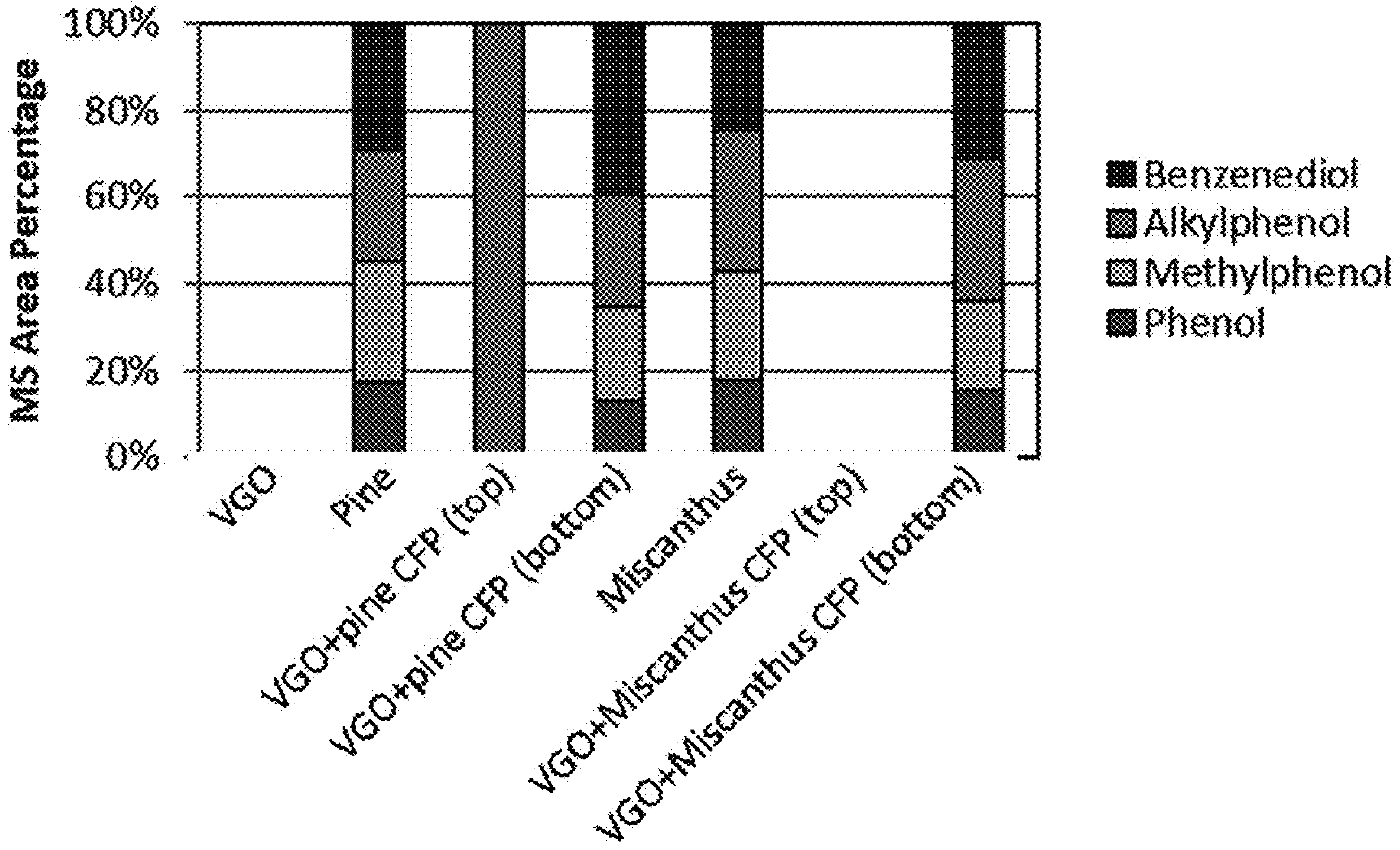

100%
80%
60%
40%
20%
0%
MS Area Percentage
VGO
Pine
VGO+pine CFP (top)
VGO+pine CFP (bottom)
Miscanthus
VGO+Miscanthus CFP (top)
VGO+Miscanthus CFP (bottom)
Benzenediol
Alkylphenol
Methylphenol
Phenol

Figure 16D

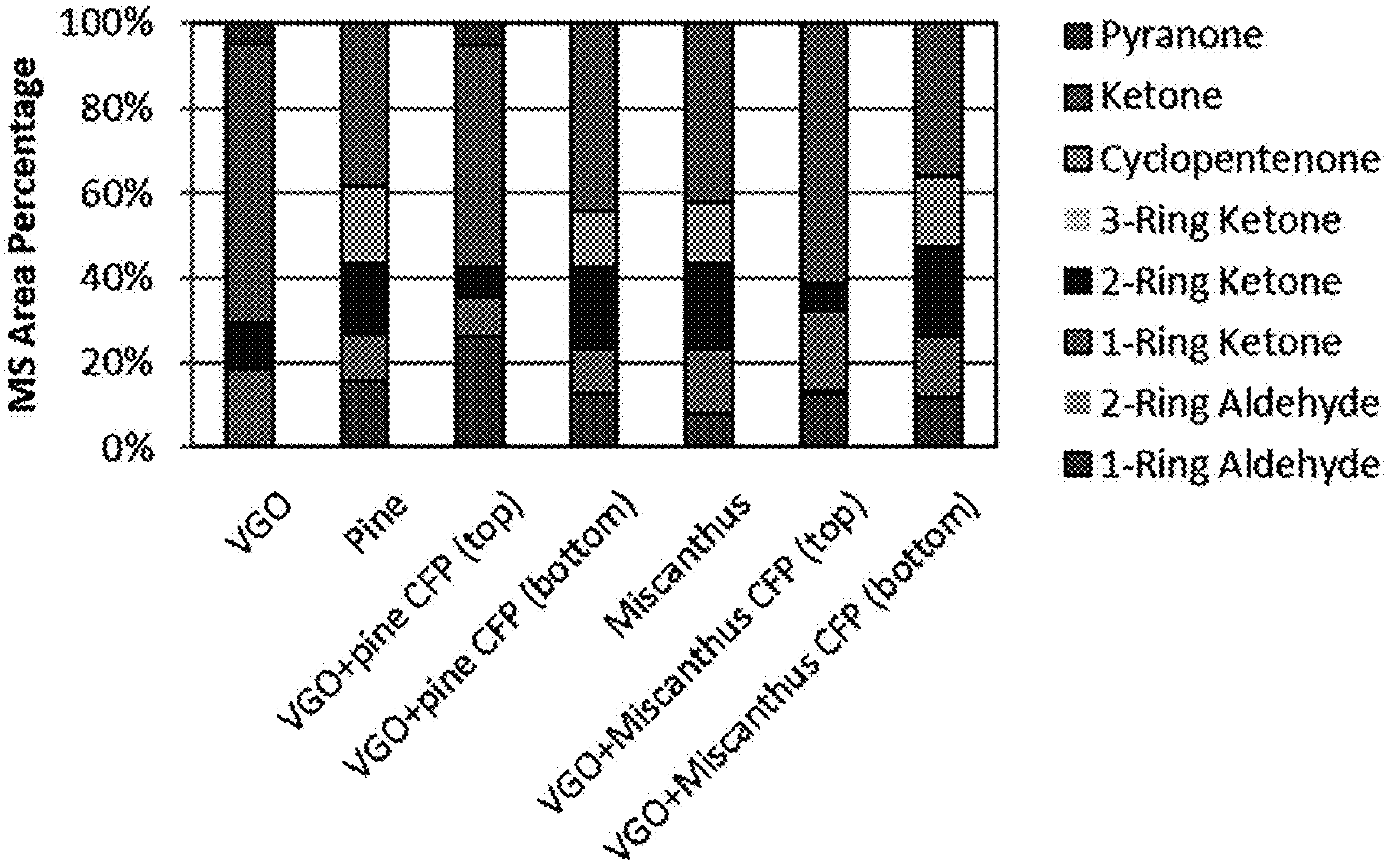

MS Area Percentage
100%
80%
60%
40%
20%
0%
VGO
Pine
VGO+pine CFP (top)
VGO+pine CFP (bottom)
Miscanthus
VGO+Miscanthus CFP (top)
VGO+Miscanthus CFP (bottom)
Pyranone
Ketone
Cyclopentenone
3-Ring Ketone
2-Ring Ketone
1-Ring Ketone
2-Ring Aldehyde
1-Ring Aldehyde

Figure 16E

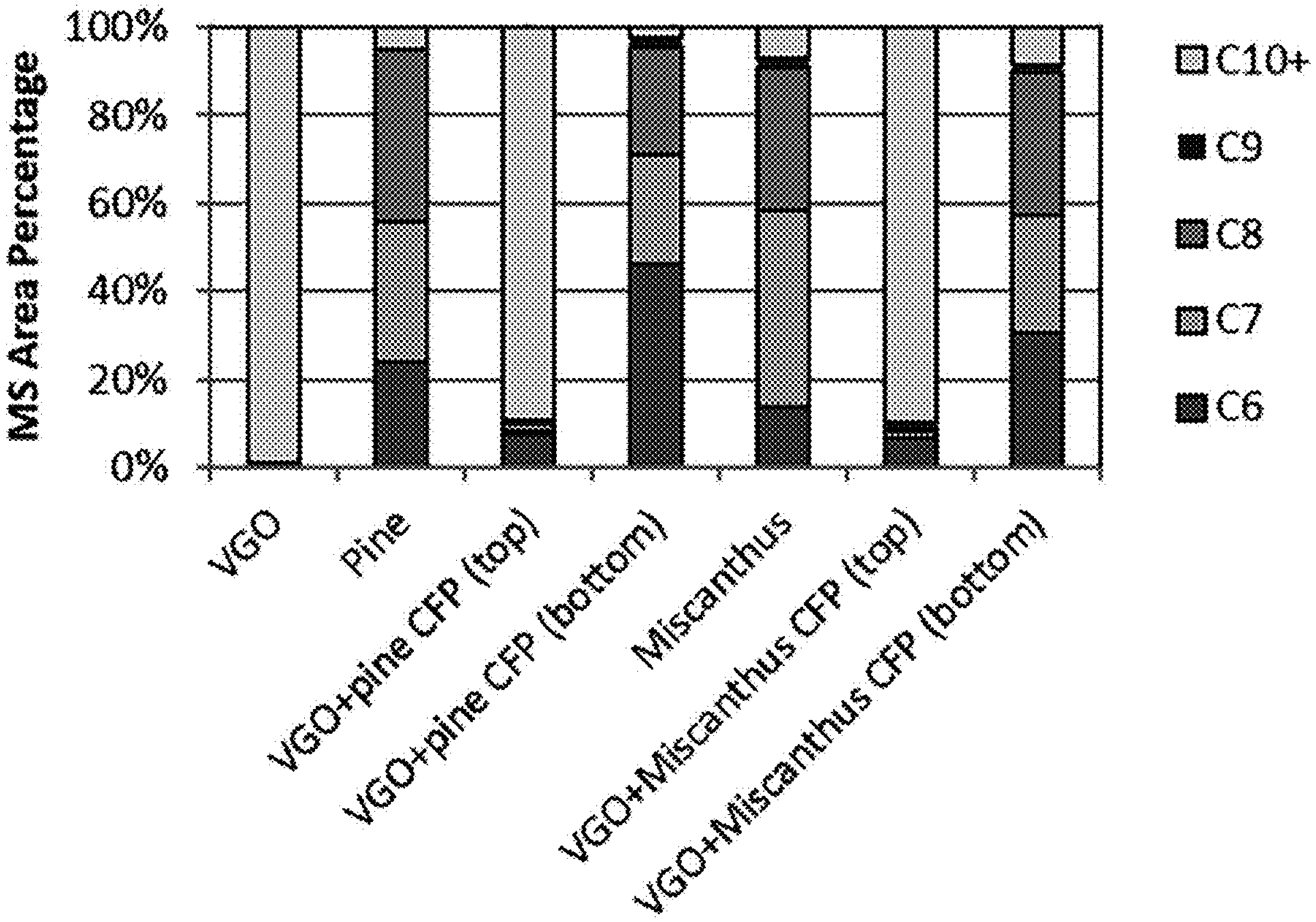

MS Area Percentage
100%
80%
60%
40%
20%
0%
VGO
Pine
VGO+pine CFP (top)
VGO+pine CFP (bottom)
Miscanthus
VGO+Miscanthus CFP (top)
VGO+Miscanthus CFP (bottom)
C10+
C9
C8
C7
C6

Figure 16F

SYSTEMS AND METHODS FOR PRODUCING FUEL INTERMEDIATES

CROSS-REFERENCE TO RELATED APPLICATIONS

[0001] This application claims the benefit of U.S. Provisional Patent Application No. 62/484,959 filed Apr. 13, 2017, the contents of which are incorporated herein by reference in their entirety.

CONTRACTUAL ORIGIN

[0002] The United States Government has rights in this disclosure under Contract No. DE-AC36-08GO28308 between the United States Department of Energy and Alliance for Sustainable Energy, LLC, the Manager and Operator of the National Renewable Energy Laboratory.

BACKGROUND

[0003] The diminishing availability of high-quality crude oils, increasing worldwide energy demand, and associated environmental issues of fuel production and use make oils from nonfood, biomass-derived resources an attractive hydrocarbon fuel feedstock option. Biofuel production from processing pure biomass-derived (bioderived) materials and/or co-processing these materials with petroleum-derived feedstocks has the potential to significantly reduce greenhouse gas emissions (GHG) through the entire fuel production process chain. However, many technical difficulties still exist before biofuels can be technically and economically viable. Thus, there remains a need for improved technological solutions for producing fuels and fuel intermediates from biomass-derived materials.

SUMMARY

[0004] An aspect of the present disclosure is a liquid composition that includes an alkane concentration between 40 wt % and 55 wt %, and an alkene concentration between greater than 0 wt % and 20 wt %, where cyclopentenone accounts for greater than 65 wt % of the alkane concentration. In some embodiments of the present disclosure, the liquid composition may further include phenol. In some embodiments of the present disclosure, at least a portion of the liquid composition may be bioderived.

[0005] An aspect of the present disclosure is a liquid composition that includes a concentration of single ring aromatics of less than 40 wt %, a concentration of two ring aromatics of less than 60 wt %, and a concentration of oxygenates of less than 20 wt %. In some embodiments of the present disclosure, greater than 70 wt % of the oxygenates may include at least one of butanone and/or butenone. In some embodiments of the present disclosure, greater than 25 wt % of the oxygenates may include pentenone. In some embodiments of the present disclosure, about 20 wt % of the oxygenates may include a methyl phenol, and about 20 wt % of the oxygenates may include an alkyl phenol. In some embodiments of the present disclosure, about 55 wt % of the oxygenates may include benzene diol. In some embodiments of the present disclosure, at least a portion of the liquid composition may be bioderived.

[0006] An aspect of the present disclosure is a method that includes thermally reacting a biomass to produce a bio-oil and upgrading the bio-oil to produce a liquid product, where the thermally reacting is performed in a pyrolysis reactor, and the upgrading is performed an upgrading reactor. In some embodiments of the present disclosure, the liquid product may include a concentration of single ring aromatics of less than 40 wt %, a concentration of two ring aromatics of less than 60 wt %, and a concentration of oxygenates of less than 20 wt %. In some embodiments of the present disclosure, the upgrading reactor may be a fluidized bed reactor. In some embodiments of the present disclosure, the pyrolysis reactor may be a catalytic fast pyrolysis reactor. In some embodiments of the present disclosure, the biomass may include at least one of a wood and/or a grass.

[0007] In some embodiments of the present disclosure, the method may further include, prior to the upgrading, combining the bio-oil with a second oil, where the upgrading further includes the second oil. In some embodiments of the present disclosure, the second oil may include at least one of a vacuum gas oil, a light cycle oil, and/or a naphthenic. In some embodiments of the present disclosure, the combining may include mechanically mixing the bio-oil and the second oil to form a suspension. In some embodiments of the present disclosure, the method may further include, before the upgrading, phase separating the suspension to form a light phase oil and a heavy phase oil. In some embodiments of the present disclosure, the upgrading may be performed on the heavy phase oil.

[0008] An aspect of the present disclosure is a method that includes thermally reacting a biomass to produce a bio-oil, mixing the bio-oil with a second oil that includes at least one of a vacuum gas oil, a light cycle oil, and/or a naphthenic to form a suspension, phase separating the suspension to form a light phase oil and a heavy phase oil, and upgrading the heavy phase oil to produce a liquid product, where the thermally reacting is performed in a pyrolysis reactor, and the upgrading is performed an upgrading reactor.

BRIEF DESCRIPTION OF THE DRAWINGS

[0009] Exemplary embodiments are illustrated in referenced figures of the drawings. It is intended that the embodiments and figures disclosed herein are to be considered illustrative rather than limiting.

[0010] FIG. **1** illustrates a system for producing liquid products, according to some embodiments of the present disclosure.

[0011] FIG. **2** illustrates a method for producing liquid products, according to some embodiments of the present disclosure.

[0012] FIG. **3** illustrates a schematic of a system that includes a Davison Circulating Riser (DCR) reactor and a pyrolysis reactor, according to some embodiments of the present disclosure. Generally, a DCR is a circulating fluid bed system with continuous catalyst regeneration.

[0013] FIGS. **4**A-**4**D illustrate 2D GCTOFMS spectra of CFP oils and VGO produced gasoline, according to some embodiments of the present disclosure. FIG. **4**A illustrates the 2D GCTOFMS spectrum for CFP oils derived from pine, followed by treatment in the upgrading reactor using CP758; FIG. **4**B illustrates the 2D GCTOFMS spectrum for VGO treated in the upgrading reactor using E-Cat; FIG. **4**C illustrates the 2D GCTOFMS spectrum for CFP oils derived from pine, followed by treatment in the upgrading reactor using CP783; and FIG. **4**D illustrates the 2D GCTOFMS spectrum for CFP oils derived from mixed hardwoods, followed by treatment in the upgrading reactor using CP758;

[0014] FIGS. **5**A-**5**F illustrate product distributions according to 2D GCTOFMS analysis resulting from different raw materials used in the pyrolysis reactor and catalyst choice in the upgrading reactor, according to some embodiments of the present disclosure. FIG. **5**A illustrates the distribution of compound classes (e.g. oxygenates, aromatics, etc.); FIG. **5**B illustrates the distribution of aromatic compounds; FIG. **5**C illustrates the distribution of oxygenates (e.g. ethers, acids, methoxies, etc.); FIG. **5**D illustrates the distribution of 1-ring aromatic hydrocarbons; FIG. **5**E illustrates the distribution of carbonyls; and FIG. **5**F illustrates the distribution of phenols.

[0015] FIG. **6** illustrates ^{31}P NMR analysis of CFP oils and upgraded VGO liquid product, according to some embodiments of the present disclosure.

[0016] FIG. **7** illustrates permanent gases produced during steady state catalytic upgrading of pine and hardwood pyrolysis vapors, according to some embodiments of the present disclosure. Pure VGO upgrading with E-Cat is shown for comparison.

[0017] FIG. **8** illustrates hydrocarbon gases produced during steady state upgrading of pine and hardwood pyrolysis vapors, according to some embodiments of the present disclosure. Pure VGO upgrading with E-Cat is shown for comparison.

[0018] FIG. **9** illustrates a thermogravimetric analysis (TGA) based simulated distillation plot (SIM DIST) of filtered pyrolysis oils from pine and mixed hardwood, upgraded pyrolysis oils, and VGO, according to some embodiments of the present disclosure.

[0019] FIG. **10** illustrates 50/50 wt % pine CFP oil mixture with VGO mixture at 50 wt % CFP oil and 50 wt % before mixing (left panel) and after mixing and phase separation (right panel). A is “pure” VGO; D is “pure” CFP oil; B is “enhanced” VGO after mixing and separating, which was experienced a 25% volume increase due to the migration of CFP components into the VGO layer; and D is the CFP oil remaining after mixing and phase separation, according to some embodiments of the present disclosure.

[0020] FIGS. **11**A, **11**B, and **11**C illustrate 2D GCTOFMS spectra: FIG. **11**A CFP oil after mixing and phase separation (C of FIG. **10**); FIG. **11**B “enhanced” VGO containing CFP compounds (B of FIG. **10**); and FIG. **11**C “pure” VGO (A of FIG. **10**), according to some embodiments of the present disclosure.

[0021] FIG. **12** illustrates the aromatics contents determined from 2D GCTOFMS data of the top and bottom layers resulting after mixing and phase separating various CFP oils (pine and *Miscanthus*) with pure VGO, according to some embodiments of the present disclosure.

[0022] FIG. **13** illustrates the furan and phenol contents determined from 2D GCTOFMS data of the top and bottom layers resulting after mixing and phase separating various CFP oils (pine and *Miscanthus*) with pure VGO, according to some embodiments of the present disclosure.

[0023] FIGS. **14**A, **14**B, and **14**C illustrate the 2D GCTOFMS data classified into compound classes (FIG. **14**A), aromatics (FIG. **14**B), and alkanes (FIG. **14**C) resulting from product upgrading according to the experiments summarized in Table 6, according to some embodiments of the present disclosure.

[0024] FIG. **15** illustrates a thermogravimetric analysis (TGA) based simulated distillation plot (SIM DIST) obtained for the various mixed-feed upgrading experiments summarized in Table 6, according to some embodiments of the present disclosure.

[0025] FIGS. **16**A-**16**F illustrate the various compound distributions as determined from 2D GCTOFMS data of the top and bottom layers resulting after mixing and phase separating various CFP oils (pine and *Miscanthus*) with pure VGO, according to some embodiments of the present disclosure; general compounds (FIG. **16**A); aromatics (FIG. **16**B); 1-ring aromatics (FIG. **16**C); phenols (FIG. **16**D); carbonyls (FIG. **16**E); and alkenes (FIG. **16**F).

REFERENCE NUMBERS

[0026] **100** . . . system
[0027] **110** . . . oil source
[0028] **115** . . . oil
[0029] **120** . . . biomass source
[0030] **125** . . . biomass
[0031] **130** . . . pyrolysis reactor
[0032] **135** . . . pyrolysis vapor
[0033] **140** . . . solids removal unit
[0034] **142** . . . impurity
[0035] **144** . . . intermediate pyrolysis vapor
[0036] **150** . . . filter
[0037] **154** . . . purified pyrolysis vapor
[0038] **160** . . . upgrading reactor
[0039] **162** . . . vapor product
[0040] **170** . . . condenser
[0041] **172** . . . liquid product
[0042] **174** . . . liquid recycle
[0043] **176** . . . mixture
[0044] **200** . . . method
[0045] **210** . . . thermal degrading
[0046] **220** . . . separating
[0047] **240** . . . upgrading
[0048] **250** . . . condensing
[0049] **260** . . . recycling
[0050] **270** . . . combining

DETAILED DESCRIPTION

[0051] The present disclosure may address one or more of the problems and deficiencies of the prior art discussed above. However, it is contemplated that some embodiments as disclosed herein may prove useful in addressing other problems and deficiencies in a number of technical areas. Therefore, the embodiments described herein should not necessarily be construed as limited to addressing any of the particular problems or deficiencies discussed herein.

[0052] The present disclosure relates to thermochemical biomass conversion with a focus on ex-situ upgrading of biomass pyrolysis vapors, also called vapor-phase upgrading (VPU), as an efficient and economical route to pyrolysis-based fuel precursors and potentially fuels and chemicals depending on catalyst choice, feedstock choice, and process conditions. In some embodiments of the present disclosure, biomass vapors were generated via fast pyrolysis (FP) and destabilizing vapor components (char, inorganics, tar aerosols) were removed by hot gas filtration with the conditioned vapors more amenable to catalytic upgrading. A Davison Circulating Riser (DCR), a petroleum industry standard for fluid catalytic cracking (FCC) catalyst evaluation, was coupled with a custom pyrolysis reactor system designed to produce consistent pyrolysis vapors as feed to the DCR.

Baseline DCR tests with an equilibrium catalyst (E-Cat) and vacuum gas oil (VGO—see Table 2 for a list of physical properties) showed that the system operated reproducibly to produce gasoline. VGO is that portion of crude oil that has an initial boiling point of 340° C. or higher at atmospheric pressure and an average molecular weight ranging from about 200 to 600 or higher. In addition, pure hardwood or softwood vapors were upgraded using a variety of catalysts comprising zeolites and modified zeolites. Oils were condensed from the upgraded vapors and analyzed with ^{31}P and ^{13}C nuclear magnetic resonance (NMR) spectroscopy, TGA based simulated distillation (SIM DIST) boiling point curve analysis, two-dimensional GC time-of-flight mass spectroscopy (2D GC TOFMS), carbonyl and ultimate analysis (CHNO) to assess oil chemistry, process induced changes, and to identify the best conditions for producing fungible product liquids. Critical oil parameters evaluated include oxygenate content and composition, carbon content and composition, carbon conversion efficiency from biomass to products, and catalyst coking rates. In some embodiments of the present disclosure, zeolite catalysts produced oils with <12% oxygenate content. These vapor phase upgrading results demonstrate the feasibility of producing refinery compatible hydrocarbon fuel intermediates entirely from biomass derived fast pyrolysis vapors using a DCR system.

[0053] Some of the embodiments described herein reduce process issues such as catalyst coking, pyrolysis oil age-induced chemical changes, and enhanced light gas production by co-feeding biomass pyrolysis liquids with VGO to produce fuels, by using modified FCC zeolite catalysts and a Davison Circulating Riser reactor to upgrade biomass fast pyrolysis vapors directly. Additionally, in some embodiments of the present disclosure, a hot gas filter may be used to remove alkali and residual char particles from raw pyrolysis vapors to produce a cleaner, stabilized feedstock for subsequent catalytic upgrading. In some embodiments of the present disclosure, the resultant condensed liquid products may be suitable as a fuel blend-stock material and/or as a liquid fuel and/or may be suitable for insertion into refining operations with oxygen contents of 10 wt % or less depending on the upgrading catalyst choice.

[0054] FIG. **1** illustrates a system **100** for producing a liquid product **172** based on the production of pyrolysis vapors from biomass **125**, such that the pyrolysis vapors are fed to and reacted in an upgrading reactor **160** to produce the liquid product **172**. In some embodiments of the present disclosure, at least a portion of the liquid product **172** may be recycled back to the upgrading reactor **160**, such that the liquid recycle **174** and the pyrolysis vapors react in the upgrading reactor to form the liquid product **172**. Thus, in some embodiments, a first liquid product may be produced, without the use of the liquid recycle **174**, and a second liquid product may be produced (e.g. with different physical and/or performance properties than the first liquid product) by the implementation of the liquid recycle **174** to the upgrading reactor **160**. In some embodiments of the present disclosure, the liquid recycle **174** may be combined with an oil **115**A to form a mixture **176**, which is then fed with the pyrolysis vapors to the upgrading reactor **160**, such that the pyrolysis vapors, the liquid recycle **174**, and the oil **115**A react in the upgrading reactor **160** to ultimately form the liquid product **172**. Thus, a third liquid product may be produced by co-feeding a liquid recycle **174** and an oil **115**A, with the pyrolysis vapors, to the upgrading reactor, such that the third liquid product has different physical and/or performance properties than the first liquid product and/or the second liquid product. In some embodiments of the present disclosure, an oil **115**B may be co-fed with the pyrolysis vapors to the upgrading reactor **160**, without the simultaneous use of a liquid recycle **174**. Thus, a fourth liquid product may be produced by co-feeding an oil **115**B, with the pyrolysis vapors, to the upgrading reactor **160**, such that the fourth liquid product has different physical and/or performance properties than the first liquid product, the second liquid product, and/or the third liquid product. Thus, in some embodiments of the present disclosure, the liquid recycle **174** from the upgrading reactor **160** may be combined with oil **115**A (e.g. VGO and/or some other liquid phase petroleum feedstock) and fed as a mixture **176** to the upgrading reactor **160**. In some embodiments of the present disclosure, the liquid recycle **174** and an oil **115**B may be fed as two distinct and separate feed streams to the upgrading reactor **160**. In some embodiments of the present disclosure, the liquid recycle **174** and a gas phase stream (e.g. pyrolysis vapors, purified and/or otherwise) may be fed as two distinct and separate feed streams to the upgrading reactor **160**. In some embodiments of the present disclosure, the liquid recycle **174** and a gas phase stream (e.g. pyrolysis vapors, purified and/or otherwise) may be mixed and fed as a mixture (not shown) to the upgrading reactor **160**. In some embodiments of the present disclosure, a pyrolysis vapor (e.g. **154**), an oil **115**B, and the liquid recycle **174** may all be co-fed as three distinct streams to the upgrading reactor **160**. In some embodiments of the present disclosure, one or more of the options described above may be performed using condensed pyrolysis vapors. Although VGO is one possible oil **115**, other feasible oils that may be used according to some embodiments of the present disclosure include light cycle oil (LCO), and/or naphthenics. Sources **110** for such oils **115** may include petroleum-based sources and/or bio-derived sources.

[0055] Referring again to FIG. **1**, a system **100** for producing a liquid product **172** may include a biomass source **120** that produces a biomass **125** that is fed to a pyrolysis reactor **130** that produces pyrolysis vapor **135**. Examples of biomass **125** that may be utilized in some embodiments of the present disclosure include agricultural waste, forest waste, and/or municipal waste with examples including bagasse, corn stover, wheat straw, hardwood and/or softwood and associated slash, demolition wood, and/or oriented strand board. Other examples of biomass **125** that may be utilized include hardwoods, softwoods, and/or various grasses (e.g. switchgrass, bamboo, elephant grass, *Miscanthus*, etc.) The biomass **125** may be directed to the pyrolysis reactor **130** such that the biomass **125** is heated, in the absence of oxygen (O_2), to the point that the biomass **125** thermally degrades to produce pyrolysis vapor **135**. The pyrolysis vapor **135** may include a large number of components in the vapor phase as well as solid materials and/or other product species (e.g. char, alkali species, and aerosols). Additionally, biomass derived syngas (CO, CO_2, H_2) from gasification could be used to enrich pyrolysis vapors with carbon species and hydrogen for upgrading as can recycling upgraded product vapors consisting of light hydrocarbon species to C_{3+} and CO_2, CO and H_2.

[0056] The vapor phase components of the pyrolysis vapor **135** may include various cellulose, hemicellulose, and/or lignin degradation products with examples including acids, alcohols, carbonyls, aldehydes, alkenes (C_3-C_{10+}), alkanes, aromatics (1-3 ring), esters, furans, ketones, oxygenates, methoxies, phenols, sugars, and nitrogen containing compounds. Specific examples of organic pyrolysis vapor compounds include acetic acid, propionic acid, ethylene glycol, hydroquinone, glyoxal, tetradecene, benzene, toluene, styrene, indene, methylindene, naphthalene, methylnaphthalene, butyrolactone, furfural, furfuryl alcohol, 1-(2-furanyl) ethanone, 4-methyl-3-penten-2-one, 2-cyclopenten-1-one, 2-methyl-2-cyclopenten-1-one, 2,3-dimethyl-2-cyclopenten-1-one, 3-methyl-2-cyclopenten-1-one, 3,4-dimethyl-2-cyclopenten-1-one, 2-hydroxy-3-methyl-2-cyclopenten-1-one, 3-ethyl-2-cyclopenten-1-one, 3-ethyl-2-hydroxy-2-cyclopentene-1-one, 2,3-dihydroxy-1H-inden-1-one, 2,2,6,6-tetramethylpiperidone, benzylnitrile, pyridinol, indole, methylindole, hydroxyacetaldehyde, acetol, 1-hydroxy-2-butanone, 4-hydroxy-4-methyl-2-pentanone, 2,3-dihydrobenzofuran, guaiacol, 2-methoxy-4-methylphenol, 4-ethyl-2-methoxyphenol, 2-methoxy-4-vinylphenol, 2-methoxy-4-vinylphenol, eugenol, isoeugenol, 2,6-dimethoxyphenol, phenol, o-cresol, 2,5-dimethylphenol, p-cresol, m-cresol, 2,4-dimethylphenol, 3,5-dimethylphenol, 4-ethylphenol, 3-ethylphenol, 2-ethylphenol, 4-ethyl-3-methyl phenol, 4-(1-methylethyl)phenol, 2-me-1,4-benzenediol, 2,3-anhydro-D-mannosan, 1,4:3,6-dianhydro-α-D-glucopyranose, and/or levoglucosan. In addition, lower molecular weight pyrolysis compounds may react with each other to produce higher molecular weight compounds, e.g. tars, multi-ring compounds like naphthalenes, and/or char. Char is a condensed carbon solid material obtained from thermochemical conversion of biomass in an oxygen-limited environment. Biochar can be used for a range of applications as an agent for soil improvement, improved resource use efficiency, remediation and/or protection against particular environmental pollution and as an avenue for greenhouse gas (GHG) mitigation. In addition, to be recognized as biochar, the material has to pass a number of material property definitions that relate both to its value (e.g., H/Corg ratios relate to the degree of charring and therefore mineralization in soil) and its safety (e.g., heavy metal content). In addition, the pyrolysis vapor **135** may include alkali and/or alkaline earth elements where alkali and alkaline earth elements include K, Na, Mg, and Ca. Alkali and alkaline earth materials play essential roles in plant metabolism and occur in organic structures or very mobile, inorganic forms. Potassium and calcium are the most common examples. These species can vaporize during pyrolysis and deposit on cooler surfaces including reactor walls and catalyst surfaces. They also can induce gas phase polymerization reactions among reactive biomass pyrolysis species. Thus, in some embodiments of the present disclosure, alkali and/or alkaline earth elements may be removed from pyrolysis vapors via hot gas filtration to provide a cleaner, stabilized vapor for catalytic upgrading. Forms can include inorganic oxides and carbonates.

[0057] The components/compounds making up the pyrolysis vapor **135** made in the pyrolysis reactor **130** can depend significantly on the type of biomass **125** used (e.g. switchgrass versus hardwood) and on the type of pyrolysis reactor **130** used. Fast pyrolysis reactors within the scope of the present disclosure include vertical and/or horizontal fluidized-bed pyrolysis reactors, where the reactors may or may not use a solid catalyst such as olivine. A biomass pyrolysis reactor system may include at least one of a feed hopper, a lock hopper, a dosing screw/hopper, and/or a fast feed screw that introduces biomass (1-2 mm particle size, 0.5-1.5 kg dose up to 5 kg/hr) into the pyrolysis reactor. The pyrolysis reactor **130** used for the work described herein included a 2" inside diameter×40" long stainless-steel pipe located between the biomass inlet and the reactor outlet. In some embodiments of the present disclosure, operating conditions were as follows: nitrogen fluidization to achieve about a 2 second biomass residence time in the pyrolysis reactor, a pyrolysis reactor temperature of about 500° C., a pyrolysis reactor pressure of 35 psig, and a biomass to nitrogen feed ratio to the pyrolysis reactor of about 0.5. A ceramic hot gas filter removed alkali and residual char particles from the produced pyrolysis vapor of which a slipstream (at 400° C.) was sent to the DCR. The primary flow of pyrolysis vapors was condensed in a spray tower with dodecane at about 25° C. and separated from the resultant liquid mixture in a horizontal phase separator. In some embodiments of the present disclosure, water and/or steam may be provided to the pyrolysis reactor **130** such that the water and/or steam react with the biomass **125** to form the pyrolysis vapor **135**.

[0058] Thus, in some embodiments of the present disclosure, the pyrolysis vapor **135** produced in the pyrolysis reactor **130** may be purified to include substantially only the organic vapor-phase components by passing the pyrolysis vapor **135** through one or more separation units. For example, referring again to FIG. **1**, the pyrolysis vapor **135** may be passed through a solids removal unit **140** to form an intermediate pyrolysis vapor **144** by removing a first impurity **142**A from the pyrolysis vapor **135**. In some embodiments of the present disclosure, the solids removal unit **140** may include at least one of a cyclone, a mechanical filter, and/or an electrostatic filter that removes material in the solid phase (e.g. char and/or unreacted biomass) from the pyrolysis vapor **135**. The intermediate pyrolysis vapor **144** may be subsequently directed to a filter **150** such that a second impurity **142**B is removed (e.g. alkali, residual char particles <10 microns (cyclones do not efficiently capture these size particles) and aerosols) to form a purified pyrolysis vapor **154**. In some embodiments of the present disclosure, a filter **150** constructed of 10 to 20 filtration grade (0.3 μm) Pall Schumalith and/or Dia-Schumalith elements was used. Such a filter **150** was typically operated at a system pressure between 20 psia and 50 psia, at a minimum gas temperature of 410° C., at a maximum differential pressure between 20 inches of H_2O and 60 inches of H_2O, a typical differential pressure of >27 inches of H_2O, and a maximum face velocity between 10 m/h and 400 m/h. This operation of the filter **150** resulted in solids collecting in a cake on the outside of the filter element. At the end of a run, or when the filter vessel was taken off-line (e.g. when pyrolysis vapors were not being directed to the filter) the element was blown back with high pressure nitrogen (200 pig) and the solids were collected at the bottom of the filter vessel. The bottom of the filter vessel was then cooled down and the bottom flange was removed to remove the solids from the system. The filter elements were able to sustain 750° C. in an oxidizing atmosphere for burning off the char. The biomass ash was left behind and back flushed out an appropriate vent when the filter vessel was taken off-line.

[0059] The purified pyrolysis vapor **154** may then be directed to the upgrading reactor **160** such that the purified pyrolysis vapor **154** reacts in the upgrading reactor **160** to form a liquid product **172**. In some embodiments of the present disclosure, the upgrading reactor **160** may be a batch reactor, a continuous reactor, and/or a semi-continuous reactor. Further, the upgrading reactor **160** may include at least one of a packed-bed reactor and/or a fluidized-bed reactor. In some embodiments of the present disclosure, the upgrading reactor **160** may include a Davison Circulating Riser (DCR). Thus, an upgrading reactor **160** may contain a solid catalyst (not shown) that promotes the reaction of the feed materials (e.g. at least one of the purified pyrolysis vapor **154**, the oil **115**, and/or the liquid recycle **174**) to produce the final liquid product **172**.

[0060] Examples of suitable solid catalysts for use in the upgrading reactor **160** include aluminosilicates. As used herein, "aluminosilicate" refers to materials containing aluminum, silicon, and oxygen. Examples of aluminosilicates include clay minerals and zeolites. Examples of clay minerals include kaolin, smectite, illite, chlorite, sepiolite, and attapulgite. A zeolite is a microporous crystalline aluminosilicate, composed of TO_4 tetrahedra, wherein T is a silicon or aluminum atom, with oxygen atoms connecting neighboring tetrahedral. The extra-framework cations in zeolites and molecular sieves are ion exchangeable. The amount of aluminum within the framework can vary over a wide range, with silicon to aluminum ratios varying from 1 to 1 to infinity to 1 for the case where the zeolite contains no aluminum, the completely siliceous form of SiO_2. As the amount of trivalent aluminum is increased in a zeolite's framework, the zeolite's physical properties may change. Cations may be placed (or deposited) onto the surfaces and/or within the pores of a zeolite and/or a molecular sieve. Examples of such ion-exchangeable cations that may be deposited onto a zeolite crystalline surface include monovalent cations such as H^+, Li^+, K^+, Rb^+, Cs^+, Ag^+, and Tl^+, divalent cations such as Cd^{2+}, Ca^{2+}, Sr^{2+}, Cu^{2+}, Pe^+, and Ba^{2+}, rare earth ions such as La^{3+}, transition metal ions such as Cr, Mo, W, Mn, Fe, Ni, Cu, Zn, Ag, Al, and Ga, having a variety of valence charges, noble metals such as Pt and Pd in the form of $Pt(NH_3)_4^{2+}$ and $Pd(NH_3)_4^{2+}$ respectively, inorganic ions such as ammonium (NH_4^+), tetramethylammonium ion (TMA), tetraethylammonium ion (TEA), tetrapropylammonium (TPA), benzyltrimethylammonium (BTMA), and C_1-C_4 mono-n-alkylammonium, and/or di-n-alkylammonium (MA, EA, PA, BA, M2A, E2A, P2A, B2A) ions.

[0061] In some embodiments of the present disclosure, the solid catalyst used in the upgrading reactor **160** may include a molecular sieve, where the term "molecular sieve" refers to crystalline aluminosilicate materials (e.g. zeolites) that incorporate other elements instead of or in addition to silicon and aluminum. For example, aluminophosphates (AlPOs) have strictly alternating AlO_2^- and PO_2^+ units, and the framework is neutral, organophilic, and nonacidic. The alternation of aluminum or phosphorus leads to structures lacking in odd-numbered rings. Substitution of phosphorus by silicon leads to silicoaluminophosphates (SAPOs), with cation-exchange abilities. Some molecular sieves may also include one or more elements and/or compounds as catalytic active sites, as described above for zeolites.

[0062] Zeolites and molecular sieves may be characterized as small, medium, or large pore types. Non-limiting examples of these zeolites/molecular sieves include the small pore zeolites/molecular sieves, AEI, AFT, APC, ATN, ATT, ATV, AWW, BIK, CAS, CHA, CHI, DAC, DDR, ED1, ER1, GOO, KFI, LEV, LOV, LTA, MON, PAU, PHI, RHO, ROG, THO, and substituted forms thereof; the medium pore zeolites/molecular sieves, AFO, AEL, EUO, HEU, FER, MEL, MFI, MTW, MTT, TON, and substituted forms thereof and the large pore zeolites/molecular sieves, including BEA, EMT, FAU, and substituted forms thereof. Other zeolites/molecular sieves include ANA, CFI, CLO, DON, GIS, LTL, MER, MOR, MWW, SOD, faujasites, pentasils, mordenite, beta, VPI, MCM, SAPO, MeAPO, ELAPO, and ELAPSO, zeolite X, zeolite Y, VPI-5, MCM-41, ZSM-5, ZSM-11, ZSM-14, ZSM-17, ZSM-18, ZSM-20, ZSM-31, ZSM-34, ZSM-41 and ZSM-46.

[0063] A zeolite may contain pores formed from 6-membered ring, 8-membered ring, 10-membered ring, 12-membered ring, 18-membered ring, and/or a larger membered ring of silicon (or aluminum) and oxygen pairs. For example, the term "8-membered ring" refers to a closed loop that is built from eight tetrahedrally coordinated silicon (or aluminum) atoms and 8 oxygen atoms. These rings form pores with characteristic diameters. By way of example 8-membered ring ZK-5 (KFI) has a characteristic pore size of about 4 Å, 10-membered ring ZSM-5 has a characteristic pore size of about 5.5 Å, and 12-membered ring beta (BEA) zeolite has a characteristic pore size of about 7.5 Å.

[0064] Solid catalysts, including zeolites and molecular sieves, may be incorporated in another material referred to herein as a "matrix" or "binder". Such matrix materials may include synthetic or naturally occurring substances as well as inorganic materials such as clay, silica and/or metal oxides. The latter may be either naturally occurring or in the form of gelatinous precipitates or gels including mixtures of silica and metal oxides. Naturally occurring clays which can be composited with zeolite and/or molecular sieves include those of the montmorillonite and kaolin families, which families include the subbentonites and the kaolins commonly known as Dixie, McNamee, Georgia and Florida clays or others in which the main mineral constituent is halloysite, kaolinite, dickite, nacrite or anauxite. Such clays can be used in the raw state as originally mined or initially subjected to calcination, acid treatment or chemical modification. In some cases, a matrix or binder may also act as a catalyst. Equilibrium catalyst (E-Cat) is a mixture of FCC catalyst material of various age and level of activity which as whole best represents the level of activity of the average catalyst mass in the reactor. Typical FCC catalyst is composed mostly of Y zeolite with or without cation exchange bound in a matrix of clay and/or metal oxides. Other FCC catalyst components, additives or promoters maybe found in the E-Cat solid mixture. These additives may include ZSM-5 zeolite containing particles that contribute to the overall catalytic activity.

[0065] Table 1 below summarizes a catalyst used in the upgrading reactor, according to some embodiments of the present disclosure. Other suitable examples include P-doped HZSM-5 zeolites, and/or metal modified zeolites (for example at least one of Ni, Ga, Cu, Pt, and/or Ru).

TABLE 1

Upgrading Reactor Catalyst Properties			
Property	E-Cat	CP758	CP783
SAR (Si:Al molar ratio)		30	30
Na (wt %)	0.2	0.1	NA

TABLE 1-continued

Upgrading Reactor Catalyst Properties

Property	E-Cat	CP758	CP783
0-20 μm (%)	0.0	2.0	1
0-40 μm (%)	5.0	10	10
Average Bulk Density (g/cc)	0.87	0.72	0.74
Average Particle Size (μm)		90	109
Surface Area (m^2/g)	174	130	90

[0066] Referring again to FIG. **1**, in some embodiments of the present disclosure purified pyrolysis vapor **154** may be fed to an upgrading reactor **160**. In some embodiments of the present disclosure, at least a portion of the pyrolysis vapor **135** (e.g. unpurified) may be fed directly to the upgrading reactor **160** and/or at least a portion of the intermediate pyrolysis vapor **144** may be fed directly to the upgrading reactor **160**. Thus, a pyrolysis vapor including at least one of the purified pyrolysis vapor **154**, the intermediate pyrolysis vapor **144**, and/or the pyrolysis vapor **135** (e.g. unpurified) may be directed to the upgrading reactor **160** for the production of the liquid product **172**. As described above, the pyrolysis vapor may be combined with at least one of an oil **115** and/or a liquid recycle **174** derived from at least a portion of the liquid product **172**. In some embodiments of the present disclosure, the pyrolysis vapor directed to the upgrading reactor **160** may be co-fed with the oil **115**B at a pyrolysis vapor to oil mass ratio of between 5:95 and 25:75, or between 10:90 and 15:85. In some embodiments of the present disclosure, the pyrolysis vapor directed to the upgrading reactor **160** may be co-fed with the liquid recycle **174** at a pyrolysis vapor to liquid recycle mass ratio between 1:1 and 20:1. In some embodiments of the present disclosure, the liquid recycle **174** may be combined with the oil **115**A to produce a mixture **176** having a liquid recycle to oil mass ratio between 0:1 and 1000:1, which may be subsequently fed to the upgrading reactor **160**. Thus, the mixture **176** and the pyrolysis vapor may be fed to the upgrading reactor **160** at a pyrolysis vapor to mixture **176** mass ratio between greater than 0:1 and 1000:1.

[0067] Table 2 provides a summary of typical VGO physical properties. Other "VGOs" may also be used in some embodiments of the present disclosure, as well as other petroleum fractions include light cycle oil (LCO) and/or kerosene.

TABLE 2

VGO Properties
VGO Properties

API (° API)	24.7
Specific Gravity	0.9059
K Factor	12.01
Refractive Index	1.5037
Average Molecular Weight (g/mol)	430
Arom Ring Carbons Ca (wt %)	17.6
Naphthenic Ring C Cn (wt %)	20.3
Paraffinic Carbons Cp (wt %)	62.1
Sulfur (wt %)	0.35
Basic Nitrogen (wt %)	0.046
Total Nitrogen (wt %)	0.14
Conradson Carbon (wt %)	0.32
Zn (ppm)	0.1

[0068] Final liquid product from the upgrading reactor will typically have at least reduced carbonyl and/or phenol contents, with an aggregate weight percent of oxygenates of less than 10 wt %. The liquid product **172** produced in the upgrading reactor **160** may initially exit the upgrading reactor **160** as a vapor product **162**, which may be subsequently condensed in a condenser **170** to produce the liquid product. In some embodiments of the present disclosure, up to 100% of the vapor product **162** may be condensed, with non-condensables venting (not shown) from the condenser.

[0069] FIG. **2** illustrates a method **200** for producing a liquid product **172** by upgrading **240** a pyrolysis vapor in an upgrading reactor as described above. As shown in FIG. **2**, the method **200** may begin with a thermal degrading **210** of a biomass **125** to produce a pyrolysis vapor **135**. The method **200** may then proceed with the separating **220** of impurities **142** (e.g. solids) contained in the pyrolysis vapor **135** to produce a purified pyrolysis vapor **154**. The separating **220** may be achieved in one or more unit operations as previously described. The method **200** may then continue with the upgrading **240** of the purified pyrolysis vapors **154** (or as described above, intermediate pyrolysis vapors and/or the pyrolysis reactor pyrolysis vapor products) to produce a vapor product **162**. As previously described, the upgrading **240** may include co-feeding at least one of an oil **115** and/or a liquid recycle **174** with a pyrolysis vapor stream. Referring again to FIG. **2**, for example, the vapor product **162** may result in a liquid product **172** by condensing **250** the vapor product **162**. A first portion of the liquid product **172**A may be diverted as a final product and a second portion of the liquid product **172**B may remain in the system by recycling **260** the second portion of the liquid product **172**B to the upgrading reactor. In some embodiments of the present disclosure, the liquid product **172**B may be used to form a mixture **176** by combining **270** an oil **115** with the liquid recycle **174**, with the mixture **176** subsequently directed to the upgrading **240** (e.g. to the upgrading reactor).

Examples

[0070] Catalysts and feedstocks: Baseline DCR operations to produce gasoline were periodically verified with standard vacuum gas oil and an equilibrium catalyst (Y-type zeolite) with 2D GC TOFMS analysis of liquid product used to measure system reproducibility. Oak-derived pyrolysis vapors were co-fed with VGO to assess the impact of pyrolysis vapor on catalyst retention during DCR upgrading to a gasoline liquid product. These results were used to determine catalyst circulation rates for pure pyrolysis vapor feeding to the DCR. Several catalysts comprising E-Cat, ZSM-5, and a phosphorous stabilized ZSM-5 and CP758 zeolite were evaluated for pure pyrolysis vapor upgrading performance. Condensed liquid products were characterized for composition to understand catalyst induced changes. Some of the zeolite catalysts used in this study minimized oxygenated products to 12 wt % or less. Table 1 above lists typical catalyst properties.

[0071] In general, the FCC catalysts are fine, spray-dried powders having a bulk density of 0.80 to 0.96 g/cm^3 and an average particle size of 60 to 100 Current FCC catalysts consist of three major components: crystalline zeolite, binder, and/or filler. Crystalline zeolite is the primary active component and can range from about 15 to 50 weight percent of the total catalyst (all three major components). Feedstocks used in this work were oak as a representative hardwood and pine as representative softwood. Their properties are shown in Table 3.

TABLE 3

Composition of woody biomass for pyrolysis experiments

Compound	Mixed Hardwoods wt %	Loblolly Pine
Total Sugars	64.59	64.17
Glucan	41.82	39.27
Xylan	14.91	7.36
Galactan	1.20	2.89
Arabinan	0.00	2.76
Mannan	6.67	11.90
Lignin	29.03	34.28
Ash	0.43	0.79
Extractives	6.52	4.40
Total	100.58	103.64

[0072] Biomass fast pyrolysis: Referring to FIG. **3**, the Vapor Phase Upgrading (VPU) system was composed of two separate units, a pyrolysis reactor and a Davison Circulating Riser (DCR), both of which can be operated independently or together in an integrated fashion. The biomass feed system included a feed hopper, a lock hopper, a dosing screw/hopper, and a fast feed screw that introduced biomass into the pyrolysis reactor (see A in FIG. **3**). A loss in weight feeder delivered biomass (between 1 mm and 2 mm particle size, between 0.5 kg and 1.5 kg dose at 30 kg/hr) into the lock hopper of the biomass feed system. The lock hopper was purged with nitrogen to remove air from the biomass and pressurized to 5 psig over the reactor pressure before the primary feed valve was opened to deliver the biomass to the dosing hopper. In the dosing hopper, the dosing screw metered the biomass onto the fast feed screw at a rate of up to 3 kg/hr into the pyrolysis reactor. The pyrolysis reactor component of the VPU consisted of a 2 inch ID (inside diameter) 316 SS pipe with a length of 40 inches between the biomass inlet and the reactor outlet (see B in FIG. **3**). The pyrolysis reactor was fluidized with nitrogen and operated with an internal temperature of 500° C. measured via a thermal well containing a multipoint thermocouple. Pressure was controlled at about 35 psig, and pressure drops across the various unit operations were monitored to ensure a positive pressure over the DCR reactor operated at about 25 psig. For the vapor upgrading experiments, the biomass to nitrogen ratio was about 0.5. A nitrogen fluidization gas flow rate was set to achieve an average residence time of 2 seconds in the pyrolysis reactor. The reactor system featured two cyclones for char removal (see C in FIG. **3**) followed by hot gas filtration to remove alkali and residual char particles (see D in FIG. **3**). A slipstream of the hot pyrolysis vapors (at about 400° C.) was directed to the DCR via a three-way diverting valve through a heated 0.25 inch OD (outside diameter), 0.035 inch wall tubing to minimize residence time and cracking of primary pyrolysis vapors. The primary flow of vapors was condensed in a spray tower with dodecane at 25° C. and separated from the resultant two-phase liquid mixture in a horizontal phase separator (see E in FIG. **3**).

[0073] Vapor catalytic cracking and upgrading: Referring to FIG. **3**, catalytic upgrading of the pyrolysis vapors generated in the pyrolysis reactor from mixed hardwood or pine feed was conducted in the Davison Circulating Riser (DCR), which consisted of three reaction vessels (regenerator, riser, and stripper) as shown in FIG. **3** (see F). The DCR was operated adiabatically, similar to industrial FCC units, and during operation the desired riser temperatures and gas and/or liquid feed rates were set once and maintained throughout an experimental run. Catalyst (about 1.8 kg) was charged into the regenerator and transferred through the system via pressure differentials. Once catalyst reaction temperature was at steady state as measured by constant riser temperature, hot filtered pyrolysis vapors were fed into the DCR via a heated transfer line (400° C.) into an injection port located at the base of the riser. The catalyst circulation rate (the only source of heat to the riser) was varied in order to maintain the desired target temperatures. Air was introduced into the regenerator for in situ catalyst regeneration, and the produced flue gas was analyzed to determine coke deposition on the catalyst. The product stream (composed of nitrogen, steam, and hydrocarbons) was sent through a fractional condenser system (composed of a heat exchanger (20° C.), an electrostatic precipitator (ESP), a cold finger (−10° C.), and a coalescing filter), then through a reflux condenser that used a countercurrent down flow of cold product liquids to scrub the product gases swept out from the catalyst steam stripper (see G in FIG. **3**). The entire condensed product was allowed to drain and separate into a hydrocarbon phase and an aqueous phase which were analyzed separately. Residual product gases were analyzed by on-line gas chromatography.

[0074] Table 4 lists ranges for the DCR parameters utilized in the experiments reported herein. For these experiments, the system pressure was set at 15 psig and the pyrolysis vapor feed rate between 170 g/hr and 240 g/hr (total feed rate of 1 kg/hr, N_2 included). The regenerator, stripper, riser outlet, and the feed pre-heater temperatures were set to 600° C., 500° C., 550° C., and 150° C., respectively.

TABLE 4

DCR operational parameters

Operating Parameter	Effective Range
Biomass feed rate	1-4 kg/hr
Riser temperature	450-600° C.
Riser pressure	1.0-3.0 atm
Stripper temperature	500-550° C.
Regenerator temperature	600-700° C.
Solid circulation rate	5.5-10 kg/hr
Solid inventory	1.5-2 kg
Fluidization gas rate	N
Vapor residence time	S

Note:
N is between 1-6 kg/hr for the pyrolyzer, and 200-800 SLPH for the DCR; S is between 1-2 seconds in the pyrolysis reactor, and between 0.5-5 seconds in the riser.

[0075] Product analysis: Condensed pyrolysis oils collected from the pyrolysis reactor and upgraded pyrolysis liquids collected from the DCR fractional condensation train were comprehensively analyzed for chemical composition with methods comprising moisture content, ultimate and proximate analysis, carbonyl content, carboxylic acid number (CAN), simulated distillation (SIM DIST), total acid number (TAN), ^{13}C NMR, ^{31}P NMR, and two dimensional gas chromatography time of flight mass spectrometry (2D GC TOFMS).

[0076] Moisture content was determined by titration with standardized Karl-Fisher reagent on a Metohm 701 KF Titrino automatic titrator. Hydranal® 5K was used as the titrant and was standardized against a NIST traceable water standard. Samples were vigorously shaken for 60 to 90 s to suspend any heavy material that had settled before aliquoting. Approximately 100 μL of oil was transferred to the KF vessel which was preconditioned to an anhydrous condition and titrated to the instrument end point. Each sample was measured in triplicate. Elemental compositions were determined by combustion analysis using a LECO TruSpec® CHN analyzer. Oxygen was determined by difference. Calibration of the CHN analyzer is with a known standard (EDTA).

[0077] The original carbonyl analysis method developed by Faix was modified to increase sample size and decrease reactant volumes. Samples were reacted with hydroxylamine hydrochloride in ethanol and the liberated hydrochloric acid was reacted with an excess triethanolamine solution. Unreacted TEA was then titrated with standardized hydrochloric acid to determine the amount of hydroxylamine hydrochloride originally consumed which was equivalent to the amount of carbonyl groups present. The estimated detection limit was near 0.1 mol carbonyl group/kg oil. The CAN was determined by pH titration with a Metrohm 842 Titrando automatic titrator using Nicolaides' method. Samples were weighed into titration cups, diluted to 40 ml with 80% ethanol/water and titrated to a pH of 13 with standardized NaOH. The acid end point was determined by the first derivative of the pH. The pKa of organic acids is not highly variable in different organic acids. Standard potassium hydrogen phthalate and salicyclic and anisic acid carboxylic acids of known concentration were used to validate the method.

[0078] ^{13}C NMR analysis was conducted by dissolving standards, oil and upgraded products samples (200 μl) in $CDCl_3$ (250 μl) with 1 mg/ml chromium (III) acetylacetonate as relaxation reagent. All ^{13}C NMR spectral data were recorded with a Bruker 600 MHz NMR spectrometer. The quantitative ^{31}P NMR measure the absolute amount of each reactive —OH group (aromatic —OH, aliphatic —OH and carboxylic —COOH) and was calibrated against known standards of reagent grade compounds. NMR frequency shift was used to identify each type of OH group.

[0079] Two-dimensional gas chromatography time of flight mass spectrometry (2D GC TOFMS) analysis was conducted with a LECO Pegasus unit equipped with a Gerstel autosampler. The non-polar configuration used was very similar to the non-polar column used for ASTM methods D6729, D2887, D3710, D5134 and D5443 but added a second polar column to provide separation of polar olefins, aromatics and oxygenates after the primary boiling point separation. For the 2D GC TOFMS analysis, the standards and samples (100 μl) were dissolved in acetonitrile for pyrolysis oil or dichloromethane for upgraded pyrolysis oils (900 μl) with added internal standards (0.3 μg/μl each α,α,α-trifluorotoluene, 2-fluoro-1,1'-biphenyl, and σ-terphenyl). This solution was then further diluted 200 μl diluted sample with 800 μl acetonitrile or dichloromethane before injection. Post-condensation product gases were analyzed using an Agilent Technologies 490 Micro gas chromatograph, using MS5A (10 m), PPQ (10 m), AlOx (10 m), and 5CB (8 m) columns.

Results

[0080] Comprehensive chemical analysis of fast pyrolysis (FP) oils, catalytic fast pyrolysis (CFP) oils, and gasoline product from VGO was used to understand how oil composition varies with feedstock and catalyst. The aqueous phase from the CFP oils were also characterized as the biogenic carbon it contains is an upgradeable source of biomass-derived fuels and chemicals. Primary oil analysis was conducted with 2D GC TOFMS and ^{31}P NMR to characterize individual species and carbon bond types, respectively. Simulated distillation (SIM DIST) was used to compare thermal behavior of the liquids. On-line gas chromatography provided permanent gas analysis of the vapor feed to the DCR and post-condensation product gas analysis. FP and CFP oils and the control gasoline product obtained from VGO and E-Cat showed significant differences as expected. FIGS. **4**A-**5**D illustrate 2D GC TOFMS spectra of the upgraded pyrolysis oils and gasoline product: liquid VGO upgrading with equilibrium catalyst (E-Cat) via the DCR system, the baseline experiment to produce gasoline, is E-Cat VGO (see FIG. **4**B); the upgrading experiments with pine (P) or mixed hardwood (MHW) fast pyrolysis vapors were conducted with the Johnson Matthey CP758 zeolite catalyst and are designated as CP758-P (see FIG. **4**A) and CP758-MHW (see FIG. **4**D); the upgrading experiment pine and the Johnson Matthey CP783 catalyst is designated as CP783-P (see FIG. **4**C). The three CFP oils were similar with hardwood producing slightly more oil than pine. The VGO product spectrum is similar to gasoline and shows characteristic hydrocarbons (paraffinics) and aromatics. The two large peaks along the upper left edge of the CFP oil spectra correspond to xylene and toluene, which selectively form with these HZSM-5-based catalysts and clearly show increased aromatic production. The absence of oxygenates seen in the upper left quadrant of each plot is notable though a few oxygenates (phenols) appear in the CP783-P spectrum.

[0081] Analyzing the more than 400 compounds present in each of these samples is complex. Compound identification from software matching, peak size, and retention times for each spectrum were tagged with CAS registry numbers to generate a searchable Excel-based spreadsheet to 1) quantitate species in the samples and 2) group compound classes. FIGS. **5**A-**5**F illustrate the compound distributions resulting from the experiments described above, resulting from an analysis of the spectral data shown in FIGS. **4**A-**4**D: general compound classes (see FIG. **5**A), aromatic compounds (see FIG. **5**B), oxygenates (see FIG. **5**C), 1-ring aromatic hydrocarbons (see FIG. **5**D), carbonyls (see FIG. **5**E), and phenols (see FIG. **5**F). Oils from both feedstocks and the CP758 catalyst are similar in composition with respect to general compound classes and aromatic hydrocarbons with significantly less alkenes/alkynes formed compared with VGO. The use of CP783 zeolite in the DCR to upgrade pine oil produced more unknown compounds and no 3-ring aromatics compared with pine oil upgraded using CP758 zeolite in the DCR as shown in FIG. **5**B. More striking is the appearance of other oxygenates comprising esters, ethers and acids, suggesting that CP783 has less deoxygenating capacity than CP758 during upgrading in the DCR (see FIG. **5**C). In addition, more alcohols and less furans were produced with the CP783 upgrading catalyst. Compared with the VGO upgraded using E-Cat, the upgraded CFP oils using CP758 and CP783 produced more 2-ring compounds and small amounts of 3-ring species.

[0082] Carbon bond types as determined by ^{31}P NMR are shown in FIG. **6** for both upgraded CFP oils and the condensed fast pyrolysis oil from unused vapors. The NMR analysis generally agreed with the 2D GC TOFMS analysis with significant increases obtained in aromatic hydrocarbons (designated as Ar. C—H) in the upgraded CFP oils compared to untreated (not upgraded) pyrolysis oils. Striking reductions in oxygenates comprising C═O and aliphatic C—O species in the CFP oils were also observed. With respect to pyrolysis reactor feedstocks and CFP oil chemistry, less C═O and aliphatic C—O containing compounds and slightly more aromatic C—O and C—C and aliphatic C—C compounds were produced with hardwood compared to pine. Hardwood derived untreated pyrolysis oil contained slightly more aromatic C—O and C—H compounds than pine derived oil, which in turn contained more aromatic C—C and aliphatic C—O species.

[0083] On-line analyses of the post-condensation gas phase products (permanent and light hydrocarbon gases) are shown in FIGS. **7** and **8** with results reported on a N_2-free basis. Permanent gas concentrations based on the upgrading of CFP were higher than those obtained from the upgrading of VGO and similar to each other, which correlates with the similar spectra shown in FIGS. **4**A-**4**D. The amount of permanent gases was similar for the various CFP runs, which also contained CO, CO_2 and CH_4 from the pyrolysis vapor feed (Table 5). As VGO does not contain oxygen, CO and CO_2 were not produced during upgrading. The VGO/E-Cat experiment showed a larger concentration of light gases (C_2-C_5) than was seen in the vapor feed experiments (see FIG. **7**). This is likely due to the higher concentration of usable carbon in VGO feed compared to the vapor feeds.

TABLE 5

Permanent gas concentration in the DCR vapor feed

Pyrolyzer Gas (vol %)	CH_4	CO	CO_2
Mixed Hardwood	1.58	4.21	2.96
Pine	1.27	3.61	2.25

[0084] Gas phase hydrocarbon species resulting from the upgraded CFP oils were predominantly C_2 and C_3 olefins with little difference observed between the various CFP feedstocks and upgrading catalysts used in the DCR. This result is consistent with the similar CFP spectra of FIGS. **4**A-**4**D. In contrast, the VGO product contained primarily C_3 and C_4 olefins along with C_4 and C_5 parafins; C_2 olefin content was similar to those found in the upgraded CFP oils. The concentration difference is attributed to the higher carbon density of the liquid VGO feed compared with the vapor carbon content. Composition difference is presumably due to the VGO feed comprising 75% of approximately equal amounts of aromatics, isoparaffins and olefins and about 25% parafins, naphthenics and other species. FIG. **9** illustrates a SIM DIST plot of filtered untreated pyrolysis oils (Pine py-oil, Mixed HW py-oil) from pine and mixed hardwood, upgraded pyrolysis oils CP758-P, CP758-HW, CP783-P), and upgraded VGO (VGO/E-Cat). SIM DIST is a simulated boiling point distribution used to characterize petroleum fractions. The simulated distillation analysis was performed on a CAHN TG-131 thermogravimetric analyzer (TGA); the sample size was nominally 250 mg. The method used was designed to duplicate the results of ASTM D86: Standard Test Method for Distillation of Petroleum Products and Liquid Fuels at Atmospheric Pressure. The D86 distillation standard was used as a reference point, and the TGA method was adjusted until the resulting weight loss curve of the D86 distillation standard matched that given by using the ASTM D86 method. SIM DIST was used to characterize VGO and its upgraded product (gasoline), raw pyrolysis oils and their upgraded products from vapor. FIG. **9** shows that 1) the three upgraded CFP oils are closer to VGO in their distillation behavior via curve shape and 2) the untreated pyrolysis oils contain more light species and less heavy species than the upgraded oils consistent with the untreated oil higher oxygenate content.

[0085] Miscibility and Characterization of Biomass Catalytic Fast Pyrolysis Liquids with Petroleum Vacuum Gas Oil (VGO): The experiments describe below investigate the miscibility of CFP oils with VGO, by mixing the two phases together and allowing them to phase separate. The mixtures were produced by mechanical mixing. In some embodiments of the present disclosure, a single liquid stream containing a first fraction of VGO and a second fraction of a CFP oil may be fed directly to an upgrading reactor, as described above, and described in more value below.

[0086] As shown in FIG. **10**, after mixing VGO with a CFP oil produced an enhanced VGO phase that contained compounds originally contained in the CFP oil. In some embodiments of the present disclosure, such an enhanced VGO phase may be fed directly to an upgrading reactor to produce biogenic carbon containing hydrocarbons.

[0087] FIGS. **11**A, **11**B, and **11**C illustrate 2D GCTOFMS spectra for some of the phases shown in FIG. **10**. FIG. **11**A illustrates the results obtained from the resultant, heavy-phase CFP oil after mixing with the lighter phase VGO and phase separation (C of FIG. **10**). FIG. **11**B illustrates the results of the resultant “enhanced” VGO, now containing CFP compounds (B of FIG. **10**). FIG. **11**C illustrates the results for the “pure” starting VGO (A of FIG. **10**), before mixing and phase separation. The “pure”, starting VGO contained characteristic short to long chain paraffinic hydrocarbons. The spectrum of the CFP-enhanced VGO clearly shows the presence of CFP oil species consisting of aromatics and longer chain hydrocarbons in the enhanced VGO. No species remaining in the phase-separated CFP phase (FIG. **11**A) appear to have migrated into the final enhanced VGO layer (FIG. **11**B). Additionally, the higher molecular weight components of this layer are phenolics and multi ring aromatics. Note that these compounds may be used as a single feedstock to an upgrading reactor and/or as a feedstock for chemicals production i.e. phenolic resins. The residual CFP oil (FIG. **11**A) still contained some of the species that migrated into the enhanced VGO layer (FIG. **11**B), suggesting that sequential extraction with VGO may further increase the amounts of biogenic species contained in the resultant enhanced VGO.

[0088] FIG. **12** focuses on the aromatics content of the 2D GCTOFS data of FIGS. **11**A-C, and including data obtained from similar experiments/analysis completed *Miscanthus*-derived CFP oils. Again, these data were collected after mixing VGO with a CFP oil and allowing phase separation to occur. The lighter enhanced VGO layers (referred to in FIG. **12** as “top”) for both feedstocks contained increased aromatics. The residual heavier CFP layers (referred to in FIG. **12** as “bottom”) also contain increased aromatics compared to pure VGO, but this is due to insufficient transfer of these compounds to the VGO. Sequential extraction of the heavier CFP layer should further increase the aromatic content of the enhanced VGO phase. FIG. **13** illustrates oxygenate migration resulted from the mixing of VGO with CFP oils. For both feedstocks (pine-derived CFP oil and

Miscanthus-derived CFP oil) furans migrated to the resultant enhanced VGO layer, while phenolics remained in the heavier CFP residual layer. This separation may be useful for preparing biogenic phenol feedstocks.

[0089] FIGS. **16**A-**16**F illustrate the various compound distributions as determined from 2D GCTOFMS data of the top and bottom layers resulting after mixing and phase separating various CFP oils (pine and *Miscanthus*) with pure VGO, according to some embodiments of the present disclosure; general compounds (see FIG. **16**A); aromatics (see FIG. **16**B); 1-ring aromatics (see FIG. **16**C); phenols (see FIG. **16**D); carbonyls (see FIG. **16**E); and alkenes see (FIG. **16**F).

[0090] VGO/CFP oil upgrading: Based on the miscibility results described above, variations of VGO, CFP/VGO mixtures and catalysts were fed to the DCR upgrading reactor to produce biogenic hydrocarbon fuels at a process relevant scale. Table 6 below lists these experiments; Run #s utilized in FIGS. **14**A-C and **15**.

TABLE 6

Pure VGO versus Mixed-Feed Upgrading Experiments

Run #	Feedstock	Catalyst
1	VGO	E-Cat
2	VGO	E-Cat/10 wt % CP758 zeolite
3A	90 wt % VGO/10 wt % CFP	E-Cat
3B	90 wt % VGO/10 wt % CFP	E-Cat
4	90 wt % enhanced VGO/ 10 wt % CFP	E-Cat/10 wt % CP758 zeolite

[0091] Upgrading reactions were completed using either pure E-Cat or a combination of 10 wt % CP758 zeolite with the remainder (90 wt %) E-Cat. These catalyst choices were used to upgrade a 10 wt % CFP-90 wt % VGO feed. VGO upgraded with E-Cat was performed as a control experiment. VGO upgraded with the catalyst mixture of zeolite/E-Cat assessed the impact of the additional catalyst on VGP product. The mixed feed was upgraded with either E-Cat as a baseline experiment or the mixed catalyst to assess impact on product composition. CFP oils from pine were produced and mixed with VGO to produce a single liquid feedstock for DCR upgrading.

[0092] FIGS. **14**A, **14**B, and **14**C illustrate the 2D GCTOFMS data classified into compound classes (FIG. **14**A), aromatics (FIG. **14**B), and alkanes (FIG. **14**C) resulting from product upgrading according to the experiments summarized in Table 6, according to some embodiments of the present disclosure. Comparing the VGO/E-Cat product with the VGO-CFP/E-Cat/zeolite product clearly shows increased aromatics and alkanes in the mixed feed mixed catalyst experiment with enhanced 1- and 2-ring aromatics and C10+ alkanes. This result is also observed in the VGO-CFP experiment conducted with E-Cat even though E-Cat is less active for converting CFP feeds. These experiments show that 10 wt % CFP oil mixed with VGO produced hydrocarbon fuels that are enriched in biogenic carbon containing alkanes and aromatics. Catalyst modifications (higher HZSM-5 content) that "tune" conversion to product slates amenable for refinery insertion (increased olefins) are possible, as is using catalysts (Pt/TiO_2) that enhance phenolics in the CFP oil for biogenic chemicals production and enhancing aromatics (toluene, xylene) for producing biogenic PET (poly ethylene terephthalate) plastics for containers.

[0093] FIG. **15** a thermogravimetric analysis (TGA) based simulated distillation plot (SIM DIST) obtained for the various mixed-feed upgrading experiments summarized in Table 6, according to some embodiments of the present disclosure. The mixed feed/mixed catalyst product clearly contains increased lower molecular weight species up to 60 wt % mass loss than the control product from VGO and E-Cat. This supports the data shown in FIGS. **11**A-**11**C and **12** that demonstrated increased aromatics and alkanes.

[0094] In some embodiments of the present disclosure, other feedstock combinations than VGO and CFP oils may be used. Other petroleum feedstocks that may be co-processed via the upgrading reactions described herein with fast pyrolysis (FP) and CFP liquids include light cycle oil (LC) and hydrocracked naphthenics. Additionally, hydrotreated FP and CFP liquids may be co-processed with these petroleum feeds. Compositionally, the most abundant constituent in LCO is aromatic compounds, especially the multi-ring aromatics. Selective hydrogenation and subsequent catalytic cracking of light cycle oil (LCO) from a fluid catalytic cracking unit is expected to produce more high-octane-number gasoline. In this process, the multi-ring aromatics are selectively hydrogenated and transformed to naphthenic aromatics, which are further converted into the gasoline fraction through cracking reaction. Naphthenic acids (NAs) are a mixture of several cyclopentyl and cyclohexyl carboxylic acids with molecular weight of 120 to well over 700 atomic mass units. The main fraction are carboxylic acids with a carbon backbone of 9 to 20 carbons. Naphthenic acids are represented by a general formula $C_nH_{2n-z}O_2$, where n indicates the carbon number and z specifies a homologous series. The z is equal to 0 for saturated, acyclic acids and increases to 2 in monocyclic naphthenic acids, to 4 in bicyclic naphthenic acids, to 6 in tricyclic acids, and to 8 in tetracyclic acids.

[0095] In summary, regarding CFP Oil compositions:

[0096] 1) Liquid CFP oils were made via biomass (pine, hardwood) fast pyrolysis vapor upgrading using an FCC riser system (upgrading reactor) with two zeolite type catalysts containing mix of Y zeolite and HZSM-5 (both proprietary Johnson Matthey catalysts);

[0097] 2) VGO was upgraded with industrially supplied E-Cat in the same system to produce baseline fuel liquid gasoline for comparison with the CFP liquids;

[0098] 3) 2D GCTOFMS shows the CFP liquids contain up to 40% more aromatics than the VGO gasoline; the CFP aromatics contain up to 50% more 2-ring aromatics compared with VGO product and up to 20% more benzene and 30% more xylene than the VGO product;

[0099] 4) CP758 increased xylene and alkyl phenol production with pine while reducing alcohol and ester formation;

[0100] 5) CP758 with both feedstocks produced up to 70% buta/enone—this is high selectivity to a single oxygenate;

[0101] 6) Pine with CP783 selectively produces up to 25% pentenone—feedstock for natural products;

[0102] 7) CFP oils have reduced oxygenate content (20%) compared with analogous FP oils (50%); CFP oxygenates comprise alcohols, carbonyls, furans and phenols for both feeds, catalysts at 10:30:30:30 ratio;

[0103] 8) Phenol content is influenced by catalyst choice: CP783 produces >50% alkylphenols compared with CFP oils from CP758, which forms ~50% methyl phenols with both feeds—provide source of biogenic phenols for polymer production;

[0104] 9) Catalyst choice (HZSM-5 content, binder, SAR, acid site strength and content) impacts CFP oil compositions: CP758 produces more xylene—green feedstock for PET production;

[0105] 10) CP758 with both feeds produces up to 70% buta/enone (oxygenate) which can be a green feedstock for varied chemicals production;

[0106] 11) Pine with CP783 selectively produces up to 25% pentenone—feedstock for natural products; and

[0107] 12) Results suggest range of zeolites to be evaluated should include >50 wt % HZSM-5.

[0108] In summary, regarding CFP/VGO miscibility:

[0109] 1) CFP oil reduced oxygenate content suggests evaluating CFP/VGO mixtures for miscibility to generate a single liquid for DCR/FCC upgrading—to address/reduce complexity of co-feeding;

[0110] 2) A 50/50 wt % mixture of VGO (less dense) and CFP oil (from pine and *Miscanthus*) (more dense) was miscible with simple mechanical stirring;

[0111] 3) Removing stirring and letting the mixture settle produced a 25% volume enhancement in the lighter VGO layer (stable with time);

[0112] 4) 2D GCTOFMS analysis of the layers showed that biogenic CFP compounds (aromatics) from both feedstocks migrated to the VGO layer with up to 20% more 2-ring aromatics than VGO;

[0113] 5) Toluene and xylene migrated to the enhanced layer for both feedstocks, benzene remained in the residual CFP layer—this has separations applications;

[0114] 6) Sequential extractions with VGO may increase CFP compound incorporation as some transferrable aromatics remain in the CFP layer;

[0115] 7) The enhanced VGO layer for both feedstocks contained increased alcohols and furans; phenols remained in the residual CFP layer—this has separations applications;

[0116] 8) Cyclopentenone remains in the residual CFP layer for both feedstocks—this is a separations application;

[0117] 9) Simple mechanical stirring of 50/50 VGO CFP mixtures produces a single feedstock for FCC upgrading—extend composition range to 10-90 wt % each component;

[0118] 10) Simple settling of the 50/50 VGO CFP (from *Miscanthus* and pine) mixture produces a stable 25% volume enhancement of the VGO layer;

[0119] 11) Enhanced VGO compositions comprise:

- **[0120]** a. Up to 20% more aromatics (1- and 2-ring compounds);
- **[0121]** b. Up to 20% more toluene and 40% more xylene; benzene remains in the residual CFP layer (separations application for recovering xylene for green PET);
- **[0122]** c. Up to 10% more alcohols and 40% more furans—with pine;
- **[0123]** d. 0% phenols; and
- **[0124]** e. Up to 25% 1-ring aldehydes both feedstocks.

[0125] 12) Residual CFP compositions comprise:

- **[0126]** a. 100% cyclopentenone and phenols—(separations applications for chemical feedstocks i.e. phenol polymers and natural products).

[0127] Regarding co-feeding CFP oils with VGO as a mixture to an upgrading reactor:

[0128] 1) CFP oils described above have 20 wt % or less oxygenates compared with fast pyrolysis oils (50 wt %);

[0129] 2) 10 wt % FP oils have been co-fed (separately) to an FCC unit before process issues begin (plugging), impact on gasoline composition per Petrobras work;

[0130] 3) Straight line correlation of inverse relation between oxygenate content and weight % co-feed yields an upper limit of 40 wt % CFP oil co-feed with VGO;

[0131] 4) The NREL produced pine-CFP/VGO mixtures were fed to an FCC unit as a single liquid feedstock (the feed mix was stirred in the feed tank)—this is process intensification with potential reduction of process cost;

[0132] 5) Baselining experiments were VGO/E-Cat for gasoline production and VGO/10 wt % CP758 zeolite and 90 wt % E-Cat to assess impact of mixed catalyst on gasoline composition;

[0133] 6) Co-fed experiments were two replicates of VGO-CFP upgraded with E-Cat only to assess mixed feed impact on gasoline product;

[0134] 7) Mixed feed/mixed catalyst (10 wt % CFP+90 wt % VGO/10 wt % CP758+90 wt % E-Cat) assessed impact of mixed feedstock with optimized catalyst mixture on liquid fuel composition;

[0135] 8) Upgraded fuel compositions showed that:

- **[0136]** a. CP758 zeolite addition to E-Cat upgraded pure VGO to contain more aromatics—this is consistent with zeolite addition to E-Cat;
- **[0137]** b. Adding CFP to VGO and upgrading with E-Cat only produced more aromatics and less alkanes—fuels from replicate experiments were identical; and
- **[0138]** c. The mixed feed/mixed catalyst (10 wt % CFP+90 wt % VGO/10 wt % CP758+90 wt % E-Cat) produced more aromatics (enhanced 2-ring species) and less alkenes/alkynes; >10% C10+ alkanes and C10+ alkenes, oxygenates in product liquids were at detection limits of the GCTOFMS.

[0139] 9) Liter amounts of pine CFP oils of 20 wt % or less oxygenates were produced by catalytic upgrading with zeolites via FCC using a coupled pyrolyzer/DCR system;

[0140] 10) A mechanically stirred mixture of 10 wt % pine-CFP+90 wt % VGO was successfully fed as a single liquid to a DCR system for FCC upgrading with variations of E-Cat and HZSM-5 mixtures to biogenic carbon containing hydrocarbon fuels;

[0141] 11) Up to 40 wt % CFP liquid (20 wt % oxygenate) may be co-fed with VGO based on extrapolating the Petrobras mixtures (50 wt % oxygenate at 10 wt % mixture with VGO);

[0142] 12) Biogenic carbon containing hydrocarbon liquids were produced from single feed upgrading experiments comprising variations of catalyst (E-Cat and HZSM-5 zeolite) and feedstock (pine-CFP oil and VGO); and

[0143] 13) Upgraded fuel compositions showed that:

- **[0144]** a. CP758 zeolite addition to E-Cat upgraded pure VGO to contain more aromatics—this is consistent with zeolite addition to E-Cat;

- **[0145]** b. Adding pine-CFP to VGO and upgrading with E-Cat only produced more aromatics and less alkanes—fuels from replicate experiments were identical. This result confirms biogenic carbon incorporation into finished fuel; and
- **[0146]** c. The mixed feed/mixed catalyst (10 wt % CFP+90 wt % VGO/10 wt % CP758+90 wt % E-Cat) produced more aromatics (enhanced 2-ring species) and 10% less alkenes/alkynes; >10% C10+ alkanes and C10+ alkenes, oxygenates in product liquids were at detection limits of the GCTOFMS.

[0147] 14) Other catalyst (metallized zeolites with M=Ga, Pt, Ru, Ag etc.), CFP (varied biomass feedstock i.e. grasses, woods, forest residues, wood wastes)/VGO combinations should provide ability to tune fuel composition properties for specific refinery needs (enhanced olefins, diesel species).

[0148] Thus, for the first time, biomass derived fast pyrolysis vapors were catalytically upgraded to >liter quantities of liquid hydrocarbon fuels, termed catalytic fast pyrolysis oils (CFP), using varied industrial zeolite catalysts (E-Cat and HZSM-5 variants), biomass feedstocks (pine and *Miscanthus*), and pilot scale FCC processing.

[0149] Produced CFP liquids contain significantly less oxygenate content (20%) compared with analogous fast pyrolysis liquids (50%) with oxygenates of interest comprising >70% buta/enone (butanone and/or butenone) in pine CFP oils and 25% pentenone in *Miscanthus* CFP oil. Other compositional differences are due to zeolite catalyst composition (varied HZSM-5 content). These compounds may be useful as feedstocks for biogenic chemicals production. CFP oils additionally contained 1-ring aromatics (benzene, toluene, xylene), which are not in FCC petroleum vacuum gas oil (VGO). Enhanced biogenic xylene is a significant feedstock for "green" PET polymer production.

[0150] The CFP oil composition (reduced oxygenates, enhanced aromatics) was shown to be miscible with VGO with simple mechanical mixing. Settling of the 50/50 vol % mixture formed a 25% volume enhanced light VGO layer and an analogous reduced volume CFP layer. Settled layer compositions were strikingly different with oxygenates remaining in the residual CFP layer. Additionally, no benzene remained in the residual *Miscanthus* CFP layer. Some toluene and xylene remain in this layer suggesting that sequential extraction with VGO would further increase their concentration in the enhanced VGO layer.

[0151] Co-processing single feed mixtures of 90 vol % 10 vol % VGO with the CFP oils and enhanced VGO layers produced gasoline with slightly higher light aromatics content. This result is significant because current state of the art uses two independent nozzles for co-feeding VGO with FP liquids to produce biogenic carbon containing fuels. Single liquid feeding is significant process intensification that likely will result in both capital and operating costs in a refinery setting. Demonstrating that CFP oil can be processed with VGO using refinery upgrading is significant in that the gasoline composition did not contain oxygenates and only slight enhancement of aromatics and alkanes. Further work with catalyst compositions and biomass feedstocks should provide "tunable i.e. enhanced olefins per refinery request" CFP feedstocks for petroleum co-processing. Further work with the residual CFP layers may result in economical separations to produce green feedstocks for chemicals production (PET from xylene, phenolic resins from phenols, natural products from furans and cyclopentenones).

[0152] Some of the observations/characteristics/properties listed above and/or described herein are summarized in Table 7 below:

TABLE 7

Experimental Summary						
Biomass Source	DCR Catalyst Type	CFP Liquid	Co-Feed CFP Liquid with VGO	Fuel Property #1	Fuel Property #2	Fuel Property #3
FCC Upgraded VGO using E-Cat and DCR System						
Baseline gasoline production via FCC	E-Cat		VGO	25% aromatics: (40% 1-ring with 0% BTX, 60% 2-ring) 15% unknown	40% alkanes: (100% C10+) 20% alkenes/alkynes	<1% oxygenates
Pure CFP Oils using Biomass Fat Pyrolysis Vapors using Zeolites and DCR system (composition ranges listed for pine CFP - Mis. CFP oil or ≤ when ranges are close)						
Pine *Miscanthus*	CP758 zeolite	Pine-CFP oil Mis.-CFP oil		≥40% 1-ring aromatics of which: 20-35% benzene 15-20% toluene 30-45% xylene ≥60% 2-ring aromatics 15-20% C6 alkanes of which: 35-45% C7 35-40% C8 3-5% C10+	<20% total oxygenates of which: 20% methyl phenols 20% alkyl phenols 55% benzene diol in pine-CFP	≤total 20% oxygenates of which: ≥70%-buta/enone in pine-CFP oil ≥25% pentenone in Mis. CFP oil

TABLE 7-continued

Experimental Summary						
Biomass Source	DCR Catalyst Type	CFP Liquid	Co-Feed CFP Liquid with VGO	Fuel Property #1	Fuel Property #2	Fuel Property #3
Pine	CP783 zeolite	Pine-CFP oil		35% 1-ring aromatics of which: 15% benzene 15% toluene 20% xylene 65% 2-ring aromatics	≥20% total oxygenates of which: 30% phenols 20% methyl phenols ≥50%-alkyl phenols	≥20% total oxygenates of which: 25% pentenone 15% buta/enone ≥40% 1-ring aldehydes
CFP/VGO Miscibility - Enhanced VGO Layer						
Pine *Miscanthus*	CP758 zeolite	50 vol % Pine CFP oil 50 vol % *Miscanthus* CFP oil	50 vol % VGO	40-55% alkanes of which: ≥65% cyclopentenone in pine-CFP oil Up to 20% alkenes in both oils	100% methyl phenol in pine-CFP oil; 0% methyl phenol in Mis.-CFP oil	
CFP/VGO Miscibility - Residual CFP Layer						
Pine *Miscanthus*	CP758 zeolite	50 vol % Pine CFP oil 50 vol % *Miscanthus* CFP oil	50 vol % VGO	10-15% aromatics in both oils of which: 30-40% 1-ring and 60-70% 2-ring; 55% benzene in pine-CFP residual 0% benzene in Mis. Residual; 5-15% toluene 20-30% xylene	>75% oxygenates in both residual CFP layers	>40% cyclopentenone
Hydrocarbon Fuels from Co-Fed CFP/VGO (single feed mixture)						
	E-Cat		100% VGO	25% aromatics: (40% 1-ring with 0% BTX, 60% 2-ring) 15% unknown	40% alkanes: (100% C10+) 20% alkenes/alkynes	<1% oxygenates
	10 wt % CP758 zeolite/90 wt % E-Cat	10 wt % pine-CFP	90 wt % VGO	40% 2-ring aromatics	10% reduction alkenes and alkynes	>10% increase in C10+ alkanes and C10+ alkenes

[0153] Whether or not a reactant or product described herein is "bioderived" or "biomass derived" may be determined by analytical methods. Using radio carbon and isotope ratio mass spectrometry analysis, the bio-based content of materials can be determined. ASTM International, formally known as the American Society for Testing and Materials, has established a standard method for assessing the biobased content of carbon-containing materials. The ASTM method is designated ASTM-D6866. The application of ASTM-D6866 to derive a "biobased content" is built on the same concepts as radiocarbon dating, but without use of the age equations. The analysis is performed by deriving a ratio of the amount of radiocarbon (14C) in an unknown sample to that of a modern reference standard. The ratio is reported as a percentage with the units "pMC" (percent modern carbon). If the material being analyzed is a mixture of present day radiocarbon and fossil carbon (containing no radiocarbon), then the pNMC value obtained correlates directly to the amount of biomass material present in the sample. Thus, ASTM-D866 may be used to validate that the compositions described herein are and/or are not derived from renewable sources.

[0154] The foregoing discussion and examples have been presented for purposes of illustration and description. The foregoing is not intended to limit the aspects, embodiments, or configurations to the form or forms disclosed herein. In the foregoing Detailed Description for example, various features of the aspects, embodiments, or configurations are grouped together in one or more embodiments, configurations, or aspects for the purpose of streamlining the disclosure. The features of the aspects, embodiments, or configurations, may be combined in alternate aspects, embodiments, or configurations other than those discussed above. This method of disclosure is not to be interpreted as reflecting an intention that the aspects, embodiments, or configurations require more features than are expressly recited in each claim. Rather, as the following claims reflect, inventive aspects lie in less than all features of a single foregoing disclosed embodiment, configuration, or aspect. While certain aspects of conventional technology have been discussed to facilitate disclosure of some embodiments of the present invention, the Applicants in no way disclaim these technical aspects, and it is contemplated that the claimed invention may encompass one or more of the conventional technical aspects discussed herein. Thus, the following claims are hereby incorporated into this Detailed Description, with each claim standing on its own as a separate aspect, embodiment, or configuration.

What is claimed is:

1. A liquid composition comprising:

an alkane concentration between 40 wt % and 55 wt %; and

an alkene concentration between greater than 0 wt % and 20 wt %, wherein:

cyclopentenone accounts for greater than 65 wt % of the alkane concentration.

2. The liquid composition of claim **1**, further comprising phenol.

3. The liquid composition of claim **1**, wherein at least a portion of the liquid composition is bioderived.

4. A liquid composition comprising:

a concentration of single ring aromatics of less than 40 wt %;

a concentration of two ring aromatics of less than 60 wt %; and

a concentration of oxygenates of less than 20 wt %.

5. The liquid composition of claim **4**, wherein greater than 70 wt % of the oxygenates comprises at least one of butanone or butenone.

6. The liquid composition of claim **4**, wherein greater than 25 wt % of the oxygenates comprises pentenone.

7. The liquid composition of claim **4**, wherein:

about 20 wt % of the oxygenates comprise a methyl phenol; and

about 20 wt % of the oxygenates comprise an alkyl phenol.

8. The liquid composition of claim **4**, wherein about 55 wt % of the oxygenates comprise benzene diol.

9. The liquid composition of claim **4**, wherein at least a portion of the liquid composition is bioderived.

10. A method comprising:

thermally reacting a biomass to produce a bio-oil; and

upgrading the bio-oil to produce a liquid product, wherein:

the thermally reacting is performed in a pyrolysis reactor, and

the upgrading is performed an upgrading reactor.

11. The method of claim **10**, wherein:

the liquid product comprises:

a concentration of single ring aromatics of less than 40 wt %;

a concentration of two ring aromatics of less than 60 wt %; and

a concentration of oxygenates of less than 20 wt %.

12. The method of claim **10**, wherein the upgrading reactor is a fluidized bed reactor.

13. The method of claim **10**, wherein the pyrolysis reactor is a catalytic fast pyrolysis reactor.

14. The method of claim **10**, wherein the biomass comprises at least one of a wood or a grass.

15. The method of claim **10**, further comprising:

prior to the upgrading, combining the bio-oil with a second oil, wherein:

the upgrading further comprises the second oil.

16. The method of claim **15**, wherein the second oil comprises at least one of a vacuum gas oil, a light cycle oil, or a naphthenic.

17. The method of claim **15**, wherein the combining comprises mechanically mixing the bio-oil and the second oil to form a suspension.

18. The method of claim **17**, further comprising:

before the upgrading, phase separating the suspension to form a light phase oil and a heavy phase oil.

19. The method of claim **18**, wherein the upgrading is performed on the heavy phase oil.

20. A method comprising:

thermally reacting a biomass to produce a bio-oil;

mixing the bio-oil with a second oil comprising at least one of a vacuum gas oil, a light cycle oil, or a naphthenic to form a suspension;

phase separating the suspension to form a light phase oil and a heavy phase oil; and

upgrading the heavy phase oil to produce a liquid product, wherein:

the thermally reacting is performed in a pyrolysis reactor, and

the upgrading is performed an upgrading reactor.

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