

Hydrodeoxygenation of Pyrolysis Oil in Supercritical Ethanol with Formic Acid as an In Situ Hydrogen Source over NiMoW Catalysts Supported on Different Materials

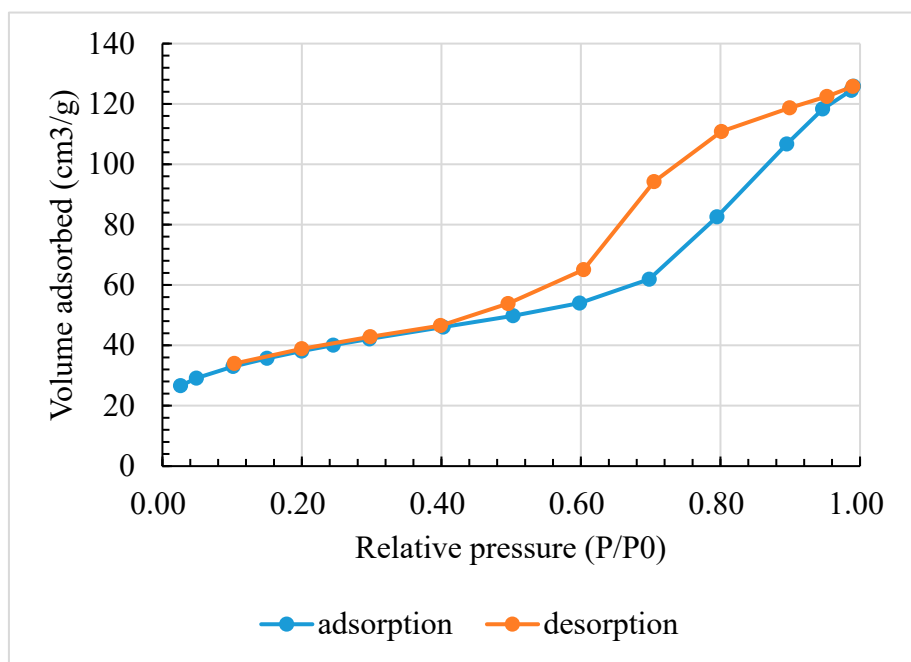
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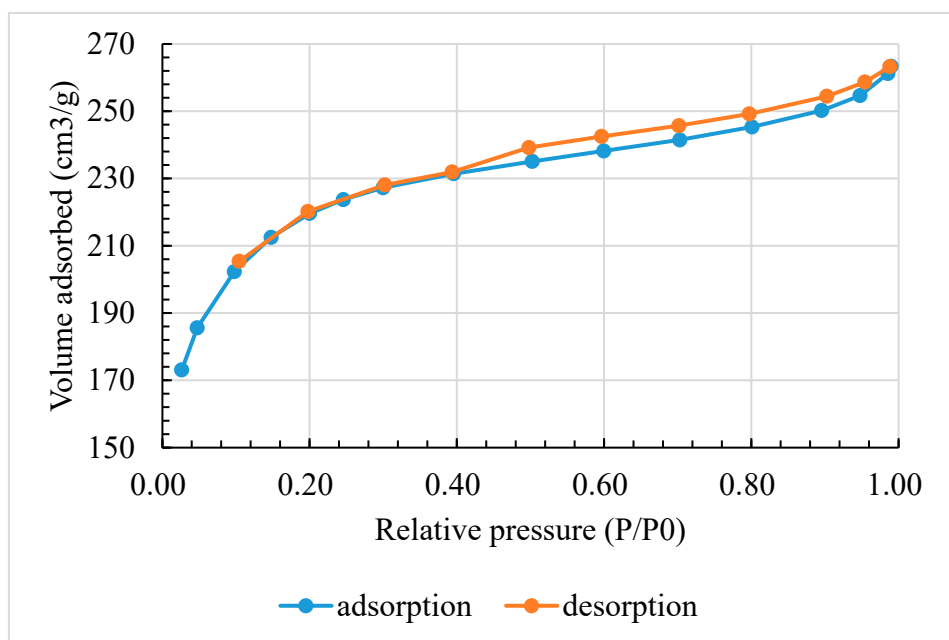
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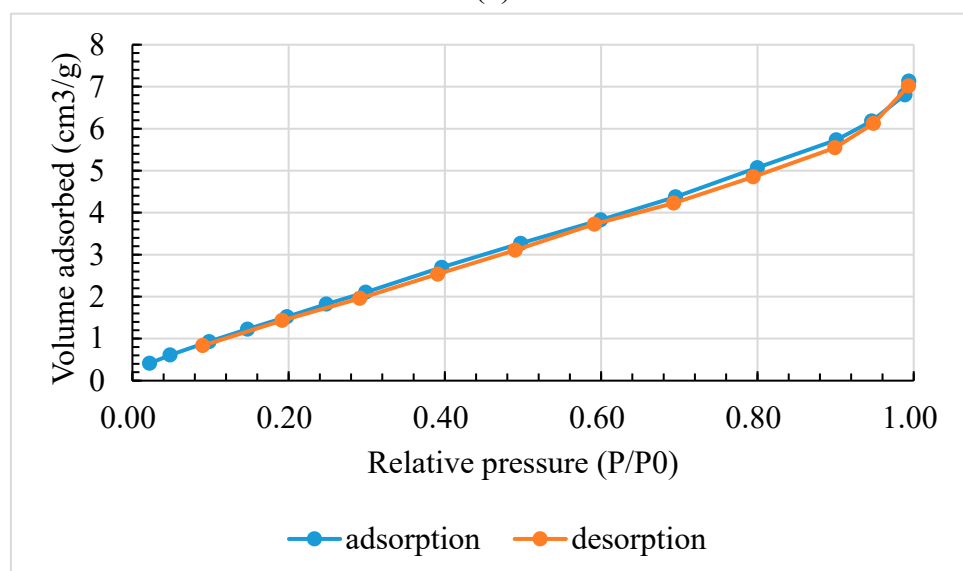
† These authors contribute equally to this work.



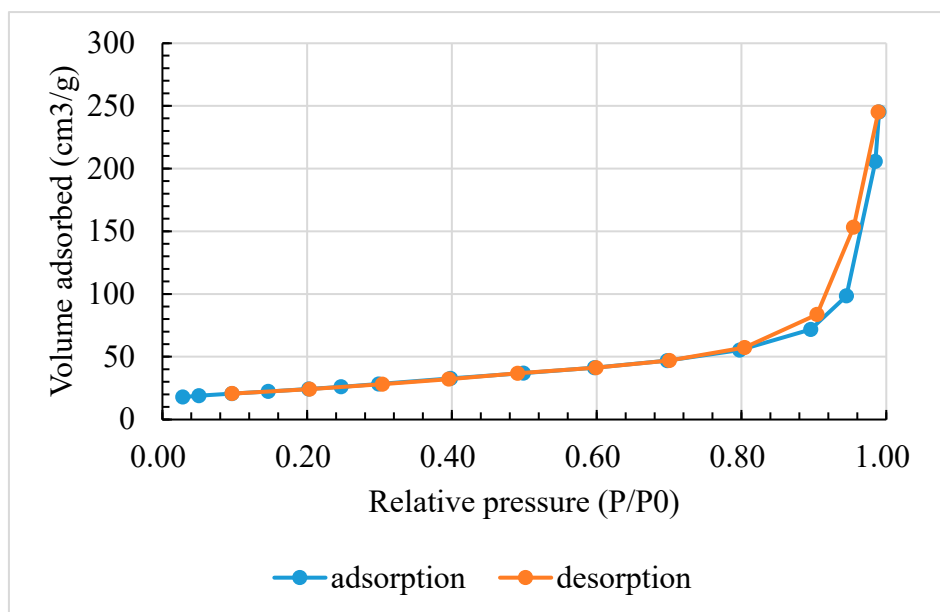
(a)



(b)



(c)



(d)

Figure S1. Nitrogen adsorption/desorption isotherms of (a) NiMoW/Al₂O₃, (b) NiMoW/AC, (c) NiMoW/SC, (d) NiMoW/MWNTs

Table S1. Organic composition of crude pyrolysis oil

Compounds	Crude pyrolysis oil
Acids	14.01
Acetic acid	6.45
3-(3,4,5-Trimethoxyphenyl)propionic acid	3.49
Dehydroabietic acid	4.07
Aldehyde	1.23
3,5-Heptadienal, 2-ethylidene-6-methyl-	1.23
Phenolics	62.59
Phenol, 2-methoxy-	8.25
Creosol	20.42
Phenol, 4-ethyl-2-methoxy-	7.40
Phenol, 2-methoxy-5-(1-propenyl)-, (E)-	6.73
Resorcinol	1.54
3-Allyl-6-methoxyphenol	6.23
Phenol, 2-methoxy-4-propyl-	5.28
trans-Isoeugenol	6.73
Ketones	8.34
2-Cyclopenten-1-one, 2-hydroxy-3-methyl-	3.46
2(3H)-Naphthalenone, 4,4a,5,6,7,8-hexahydro-1-methoxy-	1.37
Hydrocortisone	1.49
3,8,11,12,14-Pentahydroxypregn-5-en-20-one	2.02
Easters	0.00

Aromatics	0.00
Hydrocarbons	0.00
Alcohols	2.00
Olean-12-ene-3,15,16,21,22,28-hexol	2.00

Table S2. Organic composition of upgraded oil obtained over NiMoW/Al₂O₃ at 300°C with in-situ hydrogen source

Compounds	NiMoW/Al ₂ O ₃ -300°C-in situ
Acids	0.00
Aldehyde	0.00
Phenolics	45.58
Phenol, 2-methoxy-	5.72
Phenol, 2,5-dimethyl-	1.20
Creosol	17.19
1,4-Benzenediol, 2,3,5-trimethyl-	2.45
Phenol, 4-ethyl-2-methoxy-	7.50
Phenol, 2-methoxy-4-propyl-	5.84
Phenol, 2-methoxy-4-propyl-	5.68
Ketones	12.20
Ethanone, 1-(1-cyclohexen-1-yl)-	1.70
5H-Inden-5-one, 1,2,3,6,7,7a-hexahydro-7a-methyl-	2.33
Spiro[4.5]dec-6-en-8-one, 1,7-dimethyl-4-(1-methylethyl)-	1.65
2(3H)-Naphthalenone, 4,4a,5,6,7,8-hexahydro-1-methoxy-	2.57
2-(1-Cyclohexenyl)cyclohexanone	1.51
2(1H)-Naphthalenone, 1-(dimethoxymethyl)-3,4,5,6,7,8-hexahydro-	1.40
4-(3-Hydroxy-2,6,6-trimethylcyclohex-1-enyl)pent-3-en-2-one	1.05
Esters	6.49
Hexadecanoic acid, ethyl ester	1.05
Methyl abietate	1.31
Ethyl Oleate	1.15
Methyl dehydroabietate	2.99
Aromatics	16.23
Naphthalene, 1,2,3,4-tetrahydro-	10.55
1-Methyl-10,18-bisnorabieta-8,11,13-triene	1.54
Methyl dehydroabietate	2.99
Hydrocarbons	0.00
Alcohols	0.00

Table S3. Organic composition of upgraded oil obtained over NiMoW/AC at 300°C with in-situ hydrogen source

Compounds	NiMoW/AC-300°C-in situ
Acids	0.00
Aldehyde	0.00
Phenolics	71.82
Phenol	1.10
Phenol, 2-methyl-	1.08
p-Cresol	2.59
Phenol, 2-methoxy-	4.39
Phenol, 2-ethyl-	1.51
Phenol, 2,3-dimethyl-	3.38
Phenol, 2,5-dimethyl-	2.53
2-Methoxy-6-methylphenol	1.19
Phenol, 3-ethyl-5-methyl-	1.23
Creosol	6.12
Phenol, 2-ethyl-5-methyl-	2.85
Phenol, 2-ethyl-4-methyl-	2.18
Phenol, 4-ethyl-2-methyl-	3.31
Phenol, 2,3,5-trimethyl-	0.89
Phenol, 4-ethyl-2-methoxy-	5.47
Phenol, 2-ethyl-4,5-dimethyl-	1.36
2,5-Diethylphenol	2.46
Thymol	1.59
Phenol, 2,3,5,6-tetramethyl-	1.52
Phenol, 3-methoxy-2,4,5-trimethyl-	3.65
Phenol, 2-methoxy-4-propyl-	4.66
2-Ethyl-5-n-propylphenol	2.26
Benzenemethanol, 4-(1,1-dimethylethyl)-	1.95
1,4-Benzenediol, 2,3,5-trimethyl-	4.84
Phenol, 4-(3-hydroxy-1-propenyl)-2-methoxy-	1.87
Durohydroquinone	1.41
3,7-Benzofurandiol, 2,3-dihydro-2,2-dimethyl-	1.04
Phenol, 3-methoxy-2,5,6-trimethyl-	3.40
Ketones	9.31
2-Cyclopenten-1-one, 2,3-dimethyl-	0.97
Ethanone, 1-(1-cyclohexen-1-yl)-	1.09
Cyclohexene, 1,5,5-trimethyl-6-acetylmethyl	2.38
5-Acetyl-4,6,6-trimethylcyclohexa-2,4-dienone	1.38
4-(3-Hydroxy-2,6,6-trimethylcyclohex-1-enyl)pent-3-en-2-one	1.15
2,5-di-tert-Butyl-1,4-benzoquinone	2.33
Esters	1.93
Diethyl methylsuccinate	1.93

Aromatics	3.98
1-Methyl-10,18-bisnorabieta-8,11,13-triene	1.46
Retene	2.52
Hydrocarbons	0.00
Alcohols	0.00

Table S4. Organic composition of upgraded oil obtained over NiMoW/SC at 300°C with in-situ hydrogen source

Compounds	NiMoW/SC-300°C-in situ
Acids	0.00
Aldehyde	0.00
Phenolics	71.13
Phenol	0.91
Phenol, 2-methyl-	1.21
p-Cresol	2.80
Phenol, 2-methoxy-	4.45
Phenol, 2-ethyl-	1.23
Phenol, 2,4-dimethyl-	3.50
Phenol, 3-ethyl-	2.78
Phenol, 3,5-dimethyl-	2.21
Creosol	6.40
Phenol, 2-ethyl-5-methyl-	2.57
Phenol, 3-ethyl-5-methyl-	2.39
Phenol, 2-ethyl-4-methyl-	2.75
Phenol, 2,3,5-trimethyl-	1.01
Phenol, 2,4,6-trimethyl-	1.00
Phenol, 4-ethyl-2-methoxy-	6.11
2,5-Diethylphenol	2.62
Phenol, 2-methyl-5-(1-methylethyl)-	1.59
Phenol, 2,3,5,6-tetramethyl-	1.10
Phenol, 3-methoxy-2,5,6-trimethyl-	2.69
Phenol, 2-methoxy-4-propyl-	4.84
4-Ethylcatechol	2.60
Phenol, 4-(1,1-dimethylpropyl)-	1.19
1,4-Benzenediol, 2,3,5-trimethyl-	5.33
Phenol, 4-(3-hydroxy-1-propenyl)-2-methoxy-	2.46
Durohydroquinone	1.26
3,7-Benzofurandiol, 2,3-dihydro-2,2-dimethyl-	1.15
Phenol, 3-methoxy-2,5,6-trimethyl-	2.98
Ketones	8.90
2-Cyclopenten-1-one, 2,3-dimethyl-	1.01
Cyclohexanone, 2-(2-butyryl)-	1.44
2,5,5,8a-Tetramethyl-6,7,8,8a-tetrahydro-5H-chromen-3-one	1.69

1H-2-Indenone,2,4,5,6,7,7a-hexahydro-3-(1-methylethyl)-7a-methyl	2.32
5-Hydroxy-8,8-dimethyl-3,3a,4,5,6,7,8,8b-octahydroindeno[1,2-b]furan-2-one	1.09
5H-Benzo[b]pyran-8-ol, 2,3,5,5,8a-pentamethyl-6,7,8,8a-tetrahydro-	1.42
Esters	5.48
Pentanoic acid, 4-oxo-, ethyl ester	1.16
Diethyl methylsuccinate	1.69
1-Cyclohexene-1-acrylic acid, 2,6,6-trimethyl-3-oxo-, methyl ester	2.62
Aromatics	3.81
1-Methyl-10,18-bisnorabieta-8,11,13-triene	1.21
Retene	2.60
Hydrocarbons	1.10
1,3-Cyclohexadiene, 1,2,3,4,5,6-hexamethyl-	1.10
Alcohols	0.00

Table S5. Organic composition of upgraded oil obtained over NiMoW/MWNTs at 300°C with in-situ hydrogen source

Compounds	NiMoW/MWNTs-300°C-in situ
Acids	0.00
Aldehyde	0.00
Phenolics	68.10
Phenol	0.75
Phenol, 3-methyl-	0.94
p-Cresol	2.02
Phenol, 2-methoxy-	3.63
Phenol, 2-ethyl-	1.28
Phenol, 3,5-dimethyl-	3.55
Phenol, 3-ethyl-	2.37
Phenol, 3-methoxy-2-methyl-	2.10
Creosol	5.55
Phenol, 2-ethyl-5-methyl-	2.59
Phenol, 3-ethyl-5-methyl-	2.39
Phenol, 2-ethyl-4-methyl-	3.01
Phenol, 4-ethyl-2-methoxy-	5.48
2,5-Diethylphenol	2.33
Phenol, 2,3,5,6-tetramethyl-	2.46
Phenol, 4-(1-methylethyl)-	4.33
Phenol, 3-methoxy-2,4,5-trimethyl-	1.69
Phenol, 2-methoxy-4-propyl-	4.18
1,2-Benzenediol, 3,5-bis(1,1-dimethylethyl)-	3.36
1,4-Benzenediol, 2,3,5-trimethyl-	2.89

Phenol, 3-(1,1-dimethylethyl)-4-methoxy-	2.68
Phenol, 4-(3-hydroxy-1-propenyl)-2-methoxy-	1.28
Phenol, 5-methoxy-2,3,4-trimethyl-	4.31
Phenol, 3-(1,1-dimethylethyl)-4-methoxy-	1.27
Phenol, 3-ethyl-	1.68
Ketones	13.78
2-Cyclopenten-1-one, 2,3-dimethyl-	1.09
2-Cyclopenten-1-one, 3,4,4-trimethyl-	1.03
2-Butanone, 4-(2,6,6-trimethyl-1-cyclohexen-1-yl)-	1.60
2(3H)-Naphthalenone, 4,4a,5,6,7,8-hexahydro-1-methoxy-	1.81
2,5,5,8a-Tetramethyl-6,7,8,8a-tetrahydro-5H-chromen-3-one	1.60
Cyclohexene, 1,5,5-trimethyl-6-acetylmethyl-	2.09
4-Hydroxy-?-ionone	1.39
2,5,5,8a-Tetramethyl-6,7,8,8a-tetrahydro-5H-chromen-3-one	1.15
4-(3-Hydroxy-2,6,6-trimethylcyclohex-1-enyl)pent-3-en-2-one	2.03
Esters	6.65
Butanedioic acid, methyl-, dimethyl ester	1.73
1-Cyclohexene-1-acrylic acid, 2,6,6-trimethyl-3-oxo-, methyl ester	2.93
5,8,11,14-Eicosatetraynoic acid, methyl ester	1.99
Aromatics	5.04
1-Methyl-10,18-bisnorabieta-8,11,13-triene	1.77
4b,8-Dimethyl-2-isopropylphenanthrene,	1.14
4b,5,6,7,8,8a,9,10-octahydro-	
Retene	2.13
Hydrocarbons	0.00
Alcohols	0.00

Table S6. Organic composition of upgraded oil obtained over NiMoW/Al₂O₃ at 350°C with in-situ hydrogen source

Compounds	NiMoW/Al ₂ O ₃ -350°C-in situ
Acids	0.00
Aldehyde	0.00
Phenolics	66.02
Phenol	1.41
Phenol, 2-methyl-	1.96
Phenol, 3-methyl-	2.65
Phenol, 2-methoxy-	2.27
Phenol, 2-ethyl-	1.29
Phenol, 3,5-dimethyl-	3.49
Phenol, 3-ethyl-	3.07

Phenol, 2-ethyl-5-methyl-	2.11
Creosol	3.10
Phenol, 2,4,6-trimethyl-	1.18
Phenol, 2-ethyl-5-methyl-	3.44
Phenol, 3-ethyl-5-methyl-	2.92
Phenol, 3-(1-methylethyl)-	3.66
Phenol, 2,4,6-trimethyl-	0.64
Phenol, 2,3,5,6-tetramethyl-	4.79
Thymol	4.55
Phenol, 2-methyl-5-(1-methylethyl)-	2.20
2,5-Diethylphenol	3.48
2-Ethyl-5-n-propylphenol	2.35
Phenol, 2-methoxy-4-propyl-	3.24
Phenol, 2-(1,1-dimethylethyl)-5-methyl-	3.36
Phenol, 2,5-bis(1-methylethyl)-	3.03
6-tert-Butyl-2,4-dimethylphenol	1.96
Propofol	1.42
Phenol, 2-(1-methyl-2-buthenyl)-4-methoxy-	1.45
Phenol, 3,5-bis(1,1-dimethylethyl)-	0.99
Ketones	17.42
2-Cyclopenten-1-one, 2,3,4-trimethyl-	0.52
2-Cyclohexen-1-one, 3,4-dimethyl-	0.46
2-Cyclopenten-1-one, 2,3-dimethyl-	1.00
2,5,5,8a-Tetramethyl-3,5,6,7,8,8a-hexahydro-2H-naphthalen-1-one	1.51
2H-Inden-2-one, 1,4,5,6,7,7a-hexahydro-7a-methyl-, (S)-	1.46
1H-2-Indenone,2,4,5,6,7,7a-hexahydro-3-(1-methylethyl)-7a-methyl	2.65
5-Acetyl-4,6,6-trimethylcyclohexa-2,4-dienone	3.42
4-(2-Methyl-cyclohex-1-enyl)-but-3-en-2-one	3.09
2-Buten-1-one, 1-(2,6,6-trimethyl-1-cyclohexen-1-yl)-	1.37
2,5-di-tert-Butyl-1,4-benzoquinone	1.05
3-Ethyl-4,4-dimethyl-2-(2-methylpropenyl)cyclohex-2-enone	0.89
Esters	3.74
1-Cyclohexene-1-acrylic acid, 2,6,6-trimethyl-3-oxo-, methyl ester	1.55
5,8,11,14-Eicosatetraynoic acid, methyl ester	0.96
Acetic acid, 5-(2,2-dimethyl-6-oxocyclohexylidene)-3-methyl-pent-3-enyl ester	1.23
Aromatics	2.81
1-Methyl-10,18-bisnorabieta-8,11,13-triene	1.09
Retene	1.72
Hydrocarbons	1.64
1H-Indene, 1-ethylideneoctahydro-7a-methyl-, cis-	1.64

Alcohols	0.00
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Table S7. Organic composition of upgraded oil obtained over NiMoW/AC at 350°C with in-situ hydrogen source

Compounds	NiMoW/AC-350°C-in situ
Acids	0.00
Aldehyde	0.00
Phenolics	75.88
Phenol	0.99
Phenol, 2-methyl-	1.27
p-Cresol	2.85
Phenol, 2,6-dimethyl-	0.45
2-Cyclohexen-1-one, 4-ethyl-4-methyl-	1.08
Phenol, 2-ethyl-	1.98
Phenol, 3,5-dimethyl-	3.29
Phenol, 3-ethyl-	3.56
Phenol, 2,3-dimethyl-	0.60
Phenol, 3-ethyl-5-methyl-	0.95
Phenol, 3,4-dimethyl-	1.61
Phenol, 2-ethyl-5-methyl-	4.37
Phenol, 3-ethyl-5-methyl-	3.32
Phenol, 2-ethyl-6-methyl-	4.58
Phenol, 2,3,6-trimethyl-	1.34
Phenol, 2-ethyl-6-methyl-	3.25
1,4-Benzenediol, 2,5-dimethyl-	1.18
Thymol	3.16
2,5-Diethylphenol	4.88
Phenol, 2-ethyl-4,5-dimethyl-	1.39
Phenol, 3,5-diethyl-	4.53
Phenol, 2,3,5,6-tetramethyl-	3.99
Phenol, 2-(1,1-dimethylethyl)-5-methyl-	1.33
2-Ethyl-5-n-propylphenol	1.16
Phenol, 2-(1,1-dimethylethyl)-5-methyl-	4.29
Phenol, 3,5-bis(1-methylethyl)-	7.48
Propofol	3.42
6-tert-Butyl-2,4-dimethylphenol	2.70
Phenol, 2,5-bis(1-methylethyl)-	0.88
Ketones	11.24
2-Cyclopenten-1-one, 3,4,4-trimethyl-	0.54
1-Cyclohexene-1-carboxaldehyde, 2,6,6-trimethyl-	0.92
4-(2-Methyl-cyclohex-1-enyl)-but-3-en-2-one	1.35
2,5,5,8a-Tetramethyl-3,5,6,7,8,8a-hexahydro-2H-naphthalen-1-one	1.11

2-Cyclohexen-1-one, 4-hydroxy-3,5,5-trimethyl-4-(3-methyl-1,3-butadienyl)-, [S-(E)]-	1.17
2,5-di-tert-Butyl-1,4-benzoquinone	1.29
3-Buten-2-one, 4-(2,6,6-trimethyl-1-cyclohexen-1-yl)-	1.41
2,5-Cyclohexadiene-1,4-dione, 2,6-bis(1,1-dimethylethyl)-	1.01
2,3-Dehydro-4-oxo-?-ionol	1.51
3-Ethyl-4,4-dimethyl-2-(2-methylpropenyl)cyclohex-2-enone	0.94
Esters	0.00
Aromatics	2.28
Retene	2.28
Hydrocarbons	0.88
1H-Indene, 1-ethylideneoctahydro-7a-methyl-, cis-	0.88
Alcohols	0.00

Table S8. Organic composition of upgraded oil obtained over NiMoW/SC at 350°C with in-situ hydrogen source

Compounds	NiMoW/SC-350°C-in situ
Acids	0.00
Aldehyde	0.00
Phenolics	66.64
Phenol	1.43
Phenol, 2-methyl-	2.08
p-Cresol	4.07
Phenol, 2-methoxy-	2.18
Phenol, 2,5-dimethyl-	1.26
Phenol, 2-ethyl-	1.61
Phenol, 3,5-dimethyl-	4.04
Phenol, 3-ethyl-	4.71
Phenol, 2-ethyl-4-methyl-	2.13
Creosol	3.37
Phenol, 2,4,6-trimethyl-	1.24
Phenol, 2-ethyl-5-methyl-	4.10
Phenol, 3-ethyl-5-methyl-	3.28
Phenol, 2-ethyl-4-methyl-	4.72
Phenol, 2,3,5-trimethyl-	6.23
2,5-Diethylphenol	3.74
3-Methyl-4-isopropylphenol	1.45
Phenol, 4-(1-methylpropyl)-	1.98
Phenol, 2,3,5,6-tetramethyl-	3.45
Phenol, 2-methoxy-4-propyl-	6.10
Phenol, 4-(1,1-dimethylpropyl)-	1.42
Phenol, 2-(1,1-dimethylethyl)-4-methyl-	2.04
Ketones	9.74
2-Cyclopenten-1-one, 2,3-dimethyl-	0.78

2,5,5,8a-Tetramethyl-3,5,6,7,8,8a-hexahydro-2H-naphthalen-1-one	1.15
1-Butyn-3-one, 1-(6,6-dimethyl-1,2-epoxycyclohexyl)-	2.27
5-Acetyl-4,6,6-trimethylcyclohexa-2,4-dienone	3.74
2,5-di-tert-Butyl-1,4-benzoquinone	1.80
Esters	4.81
1-Cyclohexene-1-acrylic acid, 2,6,6-trimethyl-3-oxo-, methyl ester	2.01
Octadecanoic acid, ethyl ester	1.43
Hexadecanoic acid, ethyl ester	0.74
Hexadecanoic acid, ethyl ester	0.64
Aromatics	10.03
4b,8-Dimethyl-2-isopropylphenanthrene, 4b,5,6,7,8,8a,9,10-octahydro-	2.26
4b,8-Dimethyl-2-isopropylphenanthrene, 4b,5,6,7,8,8a,9,10-octahydro-	0.90
Phenanthrene, 2,7-dimethyl-	0.92
9-Ethyl-10-methylantracene	2.35
Retene	3.59
Hydrocarbons	0.00
Alcohols	0.00

Table S9. Organic composition of upgraded oil obtained over NiMoW/MWNTs at 350°C with in-situ hydrogen source

Compounds	NiMoW/MWNTs-350°C-in situ
Acids	0.00
Aldehyde	0.00
Phenolics	74.01
Phenol	1.08
Phenol, 2-methyl-	1.45
p-Cresol	3.09
Phenol, 2-ethyl-	2.04
Phenol, 3,5-dimethyl-	3.27
Phenol, 3-ethyl-	3.65
Phenol, 2,3-dimethyl-	0.58
Phenol, 3-ethyl-5-methyl-	0.93
Phenol, 3,4-dimethyl-	1.60
Phenol, 2-ethyl-5-methyl-	4.28
Phenol, 3-ethyl-5-methyl	3.38
Phenol, 2-ethyl-4-methyl-	4.79
Phenol, 2,4,6-trimethyl-	1.32
Phenol, 3,5-diethyl-	2.50
1,4-Benzenediol, 2,5-dimethyl-	1.22
2,5-Diethylphenol	4.25

Phenol, 2-methyl-5-(1-methylethyl)-	3.97
Phenol, 2-ethyl-4,5-dimethyl-	1.47
Phenol, 3,5-diethyl-	4.74
Phenol, 2,3,5,6-tetramethyl-	4.01
Phenol, 2-(1,1-dimethylethyl)-5-methyl-	2.51
Phenol, 2-(1,1-dimethylethyl)-3-methyl-	4.27
Phenol, 3,5-bis(1-methylethyl)-	5.95
Propofol	3.49
Phenol, 2,4-bis(1-methylethyl)-	2.81
2,5-di-tert-Butyl-1,4-benzoquinone	1.37
Ketones	11.70
2-Cyclopenten-1-one, 2,3,4-trimethyl-	0.65
2-Cyclohexen-1-one, 3,4-dimethyl-	0.62
2-Cyclopenten-1-one, 2,3-dimethyl-	0.73
2-Cyclohexen-1-one, 4-ethyl-4-methyl-	1.17
2-(2-Methyl-propenyl)-cyclohexanone	0.86
4-(2-Methyl-cyclohex-1-enyl)-but-3-en-2-one	1.34
2,5,5,8a-Tetramethyl-3,5,6,7,8,8a-hexahydro-2H-naphthalen-1-one	1.03
3-Buten-2-one, 4-(2,6,6-trimethyl-1-cyclohexen-1-yl)-	1.51
1H-2-Indenone,2,4,5,6,7,7a-hexahydro-3-(1-methylethyl)-7a-methyl	1.10
2,3-Dehydro-4-oxo-?-ionol	1.66
3-Ethyl-4,4-dimethyl-2-(2-methylpropenyl)cyclohex-2-enone	1.03
Easters	2.88
Carbonic acid, ethyl 4-methoxyphenyl ester	0.89
5,8,11,14-Eicosatetraynoic acid, methyl ester	0.96
Methyl abietate	1.03
Aromatics	3.76
Carbonic acid, ethyl 4-methoxyphenyl ester	0.89
5,8,11,14-Eicosatetraynoic acid, methyl ester	0.96
Methyl abietate	1.03
Hydrocarbons	0.00
Alcohols	0.00

Table S10. Organic composition of upgraded oil obtained over NiMoW/Al₂O₃ at 350°C with ex-situ hydrogen source

Compounds	NiMoW/Al ₂ O ₃ -350°C-ex situ
Acids	0.00
Aldehyde	0.00
Phenolics	63.08
Phenol	1.05
Phenol, 2-methyl-	1.31

p-Cresol	3.54
Phenol, 2-methoxy-	2.44
Phenol, 2,6-dimethyl-	0.82
Phenol, 2-ethyl-	1.40
Phenol, 2,5-dimethyl-	3.22
Phenol, 3-ethyl-	3.48
Phenol, 2,3-dimethyl-	2.24
Creosol	4.14
Phenol, 2-ethyl-5-methyl-	3.22
Phenol, 3-ethyl-5-methyl-	2.77
Phenol, 2-ethyl-4-methyl-	3.85
Phenol, 2,4,5-trimethyl-	1.05
Phenol, 4-ethyl-2-methoxy-	5.40
2,5-Diethylphenol	2.60
Phenol, 2-methyl-5-(1-methylethyl)-	2.86
Phenol, 2,3,5,6-tetramethyl-	1.26
Phenol, 3,5-diethyl-	4.35
Phenol, 2-methoxy-4-propyl-	3.10
Phenol, 2-(1,1-dimethylethyl)-5-methyl-	3.27
Propofol	2.13
Phenol, 2,5-bis(1-methylethyl)-	2.42
Phenol, 3-methoxy-2,5,6-trimethyl-	1.16
Ketones	20.49
2-Cyclopenten-1-one, 2,3-dimethyl-	2.63
4-(2-Methyl-cyclohex-1-enyl)-but-3-en-2-one	3.67
2,5,5,8a-Tetramethyl-6,7,8,8a-tetrahydro-5H-chromen-3-one	2.38
4-(2-Acetyl-5,5-dimethylcyclopent-2-enylidene)butan-2-one	2.93
1H-2-Indenone,2,4,5,6,7,7a-hexahydro-3-(1-methylethyl)-7a-methyl	1.73
2,5-di-tert-Butyl-1,4-benzoquinone	1.55
2-Buten-1-one, 1-(2,6,6-trimethyl-1-cyclohexen-1-yl)-	1.81
2,5-di-tert-Butyl-1,4-benzoquinone	1.21
3-Ethyl-4,4-dimethyl-2-(2-methylpropenyl)cyclohex-2-enone	1.06
2-Butanone, 4-(2,6,6-trimethyl-1-cyclohexen-1-yl)-	1.51
Esters	2.68
Diethyl methylsuccinate	1.49
1-Cyclohexene-1-acrylic acid, 2,6,6-trimethyl-3-oxo-, methyl ester	1.19
Aromatics	5.84
4b,8-Dimethyl-2-isopropylphenanthrene, 4b,5,6,7,8,8a,9,10-octahydro-	1.27
1-Methyl-10,18-bisnorabieta-8,11,13-triene	0.83
Retene	1.74
Naphthalene, 2-methyl-	2.00

Hydrocarbons	2.28
1,3-Cyclohexadiene, 1,2,3,4,5,6-hexamethyl-	2.28
Alcohols	2.51
2-Methyl-4-(2,6,6-trimethylcyclohex-1-enyl)but-2-en-1-ol	1.44
1-Naphthalenol, 1,2,3,4-tetrahydro-2,5,8-trimethyl-	1.07

Table S11. Organic composition of upgraded oil obtained over NiMoW/AC at 350°C with ex-situ hydrogen source

Compounds	NiMoW/AC-350°C-ex situ
Acids	0.00
Aldehyde	0.00
Phenolics	72.26
Phenol	1.90
Phenol, 2-methyl-	1.48
p-Cresol	5.64
Phenol, 2-methoxy-	2.06
Phenol, 2,6-dimethyl-	1.08
Phenol, 2-ethyl-	2.08
Phenol, 2,4-dimethyl-	3.14
Phenol, 3-ethyl-	5.46
Phenol, 2,3-dimethyl-	2.55
Creosol	4.15
Phenol, 2,4,6-trimethyl-	1.71
Phenol, 2-ethyl-5-methyl-	3.69
Phenol, 3-ethyl-5-methyl-	3.01
Phenol, 2-ethyl-4-methyl-	5.60
Phenol, 2,3,5-trimethyl-	0.97
Phenol, 2,4,6-trimethyl-	0.93
3,4-Diethylphenol	2.65
Thymol	3.41
Phenol, 2,3,5,6-tetramethyl-	1.22
Phenol, 3,5-diethyl-	4.40
Phenol, 2-methoxy-4-propyl-	5.90
1,3-Benzenediol, 4-ethyl-	2.15
2-Ethyl-5-n-propylphenol	2.07
Phenol, 2-(1,1-dimethylethyl)-5-methyl-	2.26
Propofol	1.12
Phenol, 2,5-bis(1-methylethyl)-	1.65
Ketones	4.45
5-Acetyl-4,6,6-trimethylcyclohexa-2,4-dienone	4.45
Easters	2.62
Benzene, 1-methoxy-4-(1-methylpropyl)-	1.84

1-Phenanthrenecarboxylic acid, 7-ethenyl- 1,2,3,4,4a,4b,5,6,7,9,10,10a-dodecahydro-1,4a,7-trimethyl-, ethyl ester, [1R-(1?,4a?,4b?,7?,10a?)]-	0.79
Aromatics	4.20
Naphthalene, 2-methyl-	1.49
1-Methyl-10,18-bisnorabieta-8,11,13-triene	1.03
Retene	1.69
Hydrocarbons	1.42
1H-Indene, 1-ethylideneoctahydro-7a-methyl-, cis-	1.42
Alcohols	5.51
O-Methoxy-methylbenzyl alcohol	4.36
5H-Benzo[b]pyran-8-ol, 2,3,5,5,8a-pentamethyl-6,7,8,8a- tetrahydro-	1.15

Table S12. Organic composition of upgraded oil obtained over NiMoW/SC at 350°C with ex-situ hydrogen source

Compounds	NiMoW/SC-350°C-ex situ
Acids	0.00
Aldehyde	0.00
Phenolics	74.34
Phenol	2.25
Phenol, 2-methyl-	1.55
p-Cresol	6.47
Phenol, 2-methoxy-	2.21
Phenol, 2,6-dimethyl-	0.91
Phenol, 2-ethyl-	2.05
Phenol, 2,5-dimethyl-	3.96
Phenol, 3-ethyl-	6.02
Phenol, 2,3-dimethyl-	2.39
Creosol	3.62
Phenol, 2,3,5-trimethyl-	1.49
Phenol, 2-ethyl-5-methyl-	3.34
Phenol, 4-ethyl-3-methyl-	3.05
Phenol, 3-propyl-	6.04
Phenol, 2,4,5-trimethyl-	1.01
Phenol, 2,4,6-trimethyl-	0.94
Phenol, 2-ethyl-6-methyl-	3.80
2,5-Diethylphenol	2.40
Thymol	3.06
Phenol, 2,3,5,6-tetramethyl-	1.10
Phenol, 3,5-diethyl-	4.04
Phenol, 2-methyl-5-(1-methylethyl)-	3.03
Phenol, 2-methoxy-4-propyl-	1.97
2-Ethyl-5-n-propylphenol	1.80

Phenol, 2-(1,1-dimethylethyl)-5-methyl-	1.24
2-Ethyl-5-n-propylphenol	4.62
Ketones	4.05
2-Cyclopenten-1-one, 2,3-dimethyl-	1.58
2,3-Dehydro-4-oxo-?-ionol	2.47
Esters	2.16
Octadecanoic acid, ethyl ester	1.20
Hexadecanoic acid, 2-(hexadecyloxy)ethyl ester	0.95
Aromatics	7.81
s-Indacene, 1,2,3,5,6,7-hexahydro-1,1,4,8-tetramethyl-	1.12
4b,8-Dimethyl-2-isopropylphenanthrene, 4b,5,6,7,8,8a,9,10-octahydro-	2.03
1-Methyl-10,18-bisnorabieta-8,11,13-triene	1.30
9-Ethyl-10-methylanthracene	1.27
Retene	2.10
Hydrocarbons	2.62
Bicyclo[4.4.1]undeca-1,3,5,7,9-pentaene	1.32
1H-Indene, 1-ethylideneoctahydro-7a-methyl-, cis-	1.30
Alcohols	1.93
2-Methyl-4-(2,6,6-trimethylcyclohex-1-enyl)but-2-en-1-ol	1.93

Table S13. Organic composition of upgraded oil obtained over NiMoW/MWNTs at 350°C with ex-situ hydrogen source

Compounds	NiMoW/MWNTs-350°C-ex situ
Acids	0.00
Aldehyde	0.00
Phenolics	67.03
Phenol	1.56
Phenol, 2-methyl-	0.92
p-Cresol	4.38
Phenol, 2,6-dimethyl-	0.66
Phenol, 2-ethyl-	2.63
Phenol, 2,3-dimethyl-	2.17
Phenol, 3-ethyl-	5.21
Phenol, 2,3-dimethyl-	0.69
Creosol	0.90
Phenol, 3,4-dimethyl-	1.52
Phenol, 2-ethyl-5-methyl-	4.76
Phenol, 3-ethyl-5-methyl-	3.23
Phenol, 2-ethyl-4-methyl-	5.98
Phenol, 2,4,6-trimethyl-	1.32
Phenol, 3,4,5-trimethyl-	2.44
2,5-Diethylphenol	3.16
3-Methyl-4-isopropylphenol	5.43

Phenol, 2-ethyl-4,5-dimethyl-	1.32
Phenol, 3,5-diethyl-	5.08
Phenol, 2-methyl-5-(1-methylethyl)-	4.00
Phenol, 2-(1,1-dimethylethyl)-5-methyl-	2.43
Propofol	2.52
Phenol, 3,5-bis(1-methylethyl)-	2.49
Phenol, 2,5-bis(1,1-dimethylethyl)-	1.01
Phenol, 2-(1-methyl-2-buthenyl)-4-methoxy-	1.21
Ketones	21.85
4-Cyclopentene-1,3-dione, 4-propyl-	3.03
2,5,5,8a-Tetramethyl-3,5,6,7,8,8a-hexahydro-2H-naphthalen-1-one	2.95
5-Hydroxy-8,8-dimethyl-3,3a,4,5,6,7,8,8b-octahydroindeno[1,2-b]furan-2-one	4.12
2,5-di-tert-Butyl-1,4-benzoquinone	1.32
2,3-Dehydro-4-oxo-?-ionol	3.84
3-Ethyl-4,4-dimethyl-2-(2-methylpropenyl)cyclohex-2-enone	1.24
2-Cyclopenten-1-one, 2,3-dimethyl-	5.35
Easters	0.97
8-Acetyl-5,5-dimethyl-nona-2,3,8-trienoic acid, methyl ester	0.97
Aromatics	3.85
4b,8-Dimethyl-2-isopropylphenanthrene,	1.15
4b,5,6,7,8,8a,9,10-octahydro-	
1-Methyl-10,18-bisnorabieta-8,11,13-triene	0.77
Retene	1.93
Hydrocarbons	0.00
Alcohols	1.01
1-Naphthalenol, 1,2,3,4-tetrahydro-2,5,8-trimethyl-	1.01

Table S14. All metal contents of NiMoW catalysts supported on different materials

(wt.%)	NiMoW/AC	NiMoW/SC	NiMoW/MWNTs
Al	0.0430	0.0042	0.0175
As	0.0013	0.0009	0.0016
B	0.0011	0.0006	0.0005
Ba	0.0033	0.0017	0.0003
Be	< MDL	< MDL	< MDL
Ca	0.4179	0.1656	0.0333
Cd	< MDL	< MDL	< MDL
Co	0.0098	0.0056	0.2039
Cr	0.0008	0.0011	0.0010
Cu	0.0011	0.0008	0.0003
Fe	0.0300	0.0210	0.0109

K	0.0470	0.0819	0.0032
Mg	0.0916	0.0262	0.0085
Mn	0.0258	0.0167	0.0004
Mo	2.4000	1.9888	2.8213
Na	0.0760	0.0538	0.0485
Ni	5.1913	3.9913	5.1538
P	0.0130	0.0062	0.0014
Pb	< MDL	< MDL	< MDL
S	0.3765	0.0122	0.0274
Sb	< MDL	< MDL	< MDL
Se	< MDL	< MDL	< MDL
Si	0.0337	0.0059	0.0034
Sn	< MDL	< MDL	< MDL
Sr	0.0025	0.0008	0.0003
Ti	< MDL	< MDL	< MDL
Tl	< MDL	< MDL	< MDL
V	< MDL	< MDL	< MDL
Zn	0.0018	0.0042	0.0030

< MDL: lower than method detection limit