

Supplementary Data

Table S1. Major organic compounds present in fresh and aged synthetic engine oils: (a) fresh, (b) aged at 120 °C, (c) aged at 149 °C, and (d) aged at 200 °C. The percentage match of the mass spectra of the compounds with NIST database is indicated.

Retention Time, Min	Compound Name	Percentage Match
28.013	1,7-OCTADIEN-3-OL	100
28.133	1,7-OCTADIEN-3-OL	100
28.756	DIOCTYL DISULFIDE	100
28.837	1,7-OCTADIEN-3-OL	100
29.709	1,7-OCTADIEN-3-OL	100
29.812	1,7-OCTADIEN-3-OL	100
30.404	DIOCTYL DISULFIDE	100
30.493	1,7-OCTADIEN-3-OL	100
31.418	1,7-OCTADIEN-3-OL	100
31.515	1,7-OCTADIEN-3-OL	100
31.973	DIOCTYL DISULFIDE	100
33.052	1,7-OCTADIEN-3-OL	100
33.475	1,7-OCTADIEN-3-OL	100
34.403	1,7-OCTADIEN-3-OL	100
34.52	1,7-OCTADIEN-3-OL	100
34.88	BUT-1-YN-1-YL PHENYL SELENIDE	100
35.045	1,7-OCTADIEN-3-OL	100
35.418	1,7-OCTADIEN-3-OL	100
35.94	DIOCTYL DISULFIDE	99
36.313	DIOCTYL DISULFIDE	99
36.866	1,7-OCTADIEN-3-OL	100
37.002	1,7-OCTADIEN-3-OL	100
37.295	3-METHYLENE-2-PENTANOL	88
37.647	5-BUTYLDIHYDRO-2(3H)-FURANONE	94
38.127	5-BUTYLDIHYDRO -2(3H)-FURANONE	93
38.595	7-OXANONADECANE	97
38.93	7-OXANONADECANE	87
39.517	2,3,4-PYRROLIDINETRICARBOXYLIC ACID, 5-(2-FURANYL)-2-METHYL-, TRIMETHYL ESTER,	99
40.16	4-FORMYLMETHYL-2-PROPYL-1,3-DIOXOLANE	86
40.292	1,6-OCTADIEN-3-OL, 7 METHYL-3- (TRIFLUOROMETHYL)	93
40.46	1-(BISTRIFLUOROMETHYLAMINO-OXY)-1- METHYLCYCLOHEXANE	88
41.063	TETRATRIACONTANE	85
41.396	TETRATRIACONTANE	85
47.48	CIS-2-iodo-1,3,3-TRIMETHYL CYCLOPENTANE	94
47.51	(BISTRIFLUOROMETHYLAMINO-OXY)CYCLOHEXANE	99
47.625	CIS-2-iodo-1,3,3-TRIMETHYL CYCLOPENTANE	94
47.817	1-(IODOMETHYL)-3,3-DIMETHYL CYCLOPENTANE	96

(a) Fresh synthetic oil.

Table S1. Cont.

Retention Time, Min	Compound Name	Percentage Match
29.8	DOCOSANE	90
31.398	DOCOSANE	88
31.966	DOCOSANE	85
32.065	DOCOSANE	91
32.927	METHYL-2,2-DIBUTYL BUTYRATE	86
33.58	1-(2-HYDROXYETHOXY)TRIDECANE	86
34.024	ETHYL 1-(BROMOMETHYL)-4-METHYLENECYCLOHEXANECARBOXYLATE	93
34.515	SPIRO[CYCLOPENTANE-1,2'(1' <i>H</i>)-QUINOXALINE] 3'-(4-MORPHOLINYL)-6',8'-DINITRO-	85
34.765	TETRADECYL-PHENOL ISOMER	85
35.798	TETRACOSANE/HEXADECANE	85
35.931	TETRACOSANE/HEXADECANE	86
39.529	BENZENAMINE, 4-(1,1-DIMETHYLETHYL)- <i>N</i> -(1-METHYLPROPYL)-2,6-dinitro)	87
39.731	DOTRIACONTANE	86
39.851	TETRAPENTACONTANE/PENTATRIACONTANE	87
40.18	DOTRIACONTANE	87
40.274	BENZENE, 1-[(1-ETHENYL-5-ETHOXY-2-METHOXY-4-PENTYNYL)OXY]METHYL]-4-METHOXY-	90
40.721	DOTRIACONTANE	85
40.794	DECANE, 1-iodo	85
41.068	TETRAPENTACONTANE/DOTRIACONTANE	85
41.98	DOTRIACONTANE	88
42.154	HEXACONTANE	85
42.256	TETRAPENTACONTANE/DOTRIACONTANE/HEXATRIACONTANE	87

(b) Synthetic oil aged at 120 °C.

Table S1. Cont.

Retention Time, Min	Compound Name	Percentage Match
30.396	HEXADECANE	92
32.92	3-METHYLENE-2-PENTANOL	88
33.472	7-OXANONADECANE	93
34.517	7-OXANONADECANE	96
34.766	6-BUTYL-3,5-DICHLORO-2,4-DIMETHYLPHENOL	100
35.459	α -METHOXY- α -PHENYLACETONE	86
35.79	7-OXANONADECANE	96
35.928	2-PROPYLDECAN-1-OL	85
36.66	7-OXANONADECANE	92
36.855	1,3,8-DECATRIEN-5-OL	89
37.286	1-BROMO-8-METHYLHEXACOSANE	86
38.12	1-IODOTETRADECANE	85
39.522	(2R,3S,4S,5R)-3,4-BIS[(METHOXYMETHYL)OXY]-5-(p-METHOXYPHENYL)-5-(1,3-DIOXO-2-AZIDAN-2-YL)-2-PENTANOL	76
39.605	BICYCLO[3.1.0]HEXANE-2-METHANOL	81
40.261	2,4-DIETHOXY-7-(P-HYDROXYPHENYL CARBOXYL)-8,9-EPOXY-9-(HYDROXYMETHYL)3-OXA-BICYCLO[4.3.0]-CYCLONONANE	
41.075	TETRAPENTACONTANE/DOTRIACONTANE	86

(c) Synthetic oil aged at 149 °C.

Retention Time, Min	Compound Name	Percentage Match
34.76	6-BUTYL-3,5-DICHLORO-4-DIMETHYL PHENOL	100
36.918	ETHYL 1-(BROMOMETHYL)-4-METHYLENECYCLOHEXANECARBOXYLATE	90
37.15	PENTADECANE	95
38.455	7-OXANONADECANE	96
38.785	BENZYL DICHLOROMETHYL SULFONE	86
39.511	4-(2-HYDROXYBENZYLIDENE)-1H-[2]BENZOPYRAN-1,3-Dione	97
40.16	1-BROMO-8-METHYLHEXACOSANE	85
40.257	BENZENECARBOXIMIDIC ACID, N-(METHOXYPHENYLMETHYL)-1-METHYLETHYL ESTER	90
40.865	HEXADECANE	85
41.135	2-METHYLTETRAHYDROPYRIDIN-1-YL(R)-METHOXY(TRIFLUOROMETHYL)PHENYLACETIC ACID ESTER	95
42.42	6H-1,2,5-OXADIAZOCIN-6-ONE, 3-(DIMETHYLAMINO)-4,5,7,8-TETRAHYDRO-4,4,7,7-TETRAMETHYL	87
45.315	BENZENE, 1-METHYL-4-(METHYL-D-SULFINYL)-	92
46.852	NON-2-ENOIC ANHYDRIDE	92
47.037	BICYCLO[2.2.1]HEPTAN-2-AMINE,3,3-DIMETHYL	85
50.2	3,3-ETHYLENEDIOXY-5.BETA.-ANDROSTAN-16. α -OL	88
51.655	2,2,4-TRIMETHYL-2H-IMIDAZOLE	94
51.718	CIS-3-(ETHOXYCARBONYL)-2,4-DIMETHYL-4-PENTANOLIDE	93
51.837	CIS-3-(ETHOXYCARBONYL)-2,4-DIMETHYL-4-PENTANOLIDE	95

Table S1. *Cont.*

51.925	1-(IODOMETHYL)-3,3-DIMETHYLCYCLOPENTANE	97
53.68	BENZYL DICHLOROMETHYL SULFONE	88

(d) Synthetic oil aged at 200 °C.

Table S2. Major organic compounds present in fresh and aged semi-synthetic engine oils: (a) fresh, (b) aged at 120 °C, (c) aged at 149 °C, and (d) aged at 200 °C. The percentage match of the mass spectra of the compounds with NIST database is indicated.

Retention Time, Min	Compound Name	Percentage Match
32.886	PENTADECANE	94
33.483	DISULFIDE, DIOCTYL	100
33.97	DOCOSANE	92
34.371	HEXADECANE	93
34.885	2-METHOXYCARBONYL-3,4-DICYANO-5-PHENYL-3,4,5,6-TETRAHYDRO-PYRROLE	96
34.93	1,4-BUTANEDIOL,2,3-DIETHYL-2,3-DIMETHYL-	88
35.051	OCTADECANE	89
35.121	1,4-BUTANEDIOL,2,3-DIETHYL-2,3-DIMETHYL-	87
35.218	1,4-BUTANEDIOL,2,3-DIETHYL-2,3-DIMETHYL-	88
35.291	1,4-BUTANEDIOL,2,3-DIETHYL-2,3-DIMETHYL-	87
35.42	TETRACOSANE	85
35.506	2-PROPANONE, 1-[(3-METHYL-2-BUTENYL)OXY]-	85
35.739	ETHANONE, 1-(3-ETHYLOXIRANYL)-	86
35.8	DOCOSANE	89
36.315	SULFUROUS ACID, 2-ETHYLHEXYL ISOHEXYL ESTER	76
36.443	HEXANE,4-TETRAETHYL-	85
38.265	FUMARIC ACID, OCTADECYL TRANS-HEX-3-ENYL ESTER	86
40.186	HEXADECANE,2,6,10,14-TETRAMETHYL-	86
41.465	2-CYANOCYCLOPENTANONE	86
42.701	1,3,3-TRIMETHYLAZETIDINE-2,4-DIONE	94
44.695	ETHENYL 4-PENTYNOATE	89

(a) Fresh semi-synthetic oil.

Retention Time, Min	Compound Name	Percentage Match
33.468	1-IODOTETRADECANE	85
35.97	1-HEPTACOSANOL	86
36.325	HEXATRIACONTANE/DOTRIACONTANE	85
36.813	1,54-DIBROMOTETRAPENTACONTANE	85
37.672	HEXATRIACONTANE	86
38.17	1,54-DIBROMOTETRAPENTACONTANE	88
38.637	TETRAPENTACONTANE/DOTRIACONTANE	87
39.886	TETRAPENTACONTANE/DOTRIACONTANE	87
41.104	TETRAPENTACONTANE/DOTRIACONTANE	86
41.411	HEXATRIACONTANE	88

Table S2. Cont.

42.57	HEXATRIACONTANE	87
43.664	TETRAPENTACONTANE	86
44.74	TETRAPENTACONTANE	88

(b) Semi-synthetic oil aged at 120 °C.

Retention Time, Min	Compound Name	Percentage Match
32.878	HEXADECANE	92
33.956	CYCLOHEXANE, (1-DECYLUNDECYL)-	81
34.365	DECANE, 1-iodo	86
34.518	1-(HEXADECYLOXY)ETHYLENE	85
34.6	1-(HEXADECYLOXY)ETHYLENE	81
34.765	PYRIDINE, 2,3,4,5-TETRAMETHYL-6-PHENYL	98
34.963	1-iodotetradecane	81
35.047	2,2-DIMETHYL-3-OCTANONE	80
35.115	HEXANAL, 3,3-DIMETHYL	82
35.209	HEXANE, 3,3,4-TRIMETHYL	81
35.287	2,2-DIMETHYL-3-OCTANONE	83
35.362	CYCLOPROPANE, 1-METHYL-1-(1-METHYLETHYL)-2-NONYL-	78
35.417	TETRACOSANE/HEXADECANE	83
35.796	HEXADECANE	82
35.969	7-CYCLOHEXYLTRIDECANE	82
36.118	4-METHYLDODOCOSANE	69
36.315	NONADECANE/TRITRIACONTANE / HEINECOSANE	83
36.36	1-(2-HYDROXYETHYL)-5-METHYL-2,4(1H, 3H)-PYRIMIDINEDIONE	66
36.44	3,9-DIMETHYL UNDECANE	80
36.517	5,6-DIMETHYL DECANE	69
36.607	DODECANE, 2,6,10-TRIMETHYL	80
36.694	CYCLOHEXANE, (1-DECYLUNDECYL)-/CARBONIC ACID, BUTYL PENTADECYL ESTER	73
36.804	TETRAPENTACONTANE, 1,54-DIBROMO	84
36.885	FUMARIC ACID, OCTADECYL TRANS-HEX-3-ENYL ESTER	78
36.982	(1-METHYLUNDECYL)CYCLOHEXANE	76
37.085	MALONIC ACID, ISOBUTYL TETRADECYL ESTER	74
37.174	2-BROMOTETRADECANE	78
37.245	6-(HYDROXYMETHYL)-1,3-DIMETHYLDIHYDRO-2,4(1H,3H)-PYRIMIDINEDIONE	79
37.314	HEXADECANE, 2,6,10,14-TETRAMETHYL	84
37.379	1-EICOSANOL/1-HEPTACOSANOL/1-OCTACOSANOL	81
37.442	(1-PROPYLDECYL)CYCLOHEXANE	83
37.519	TETRAPENTACONTANE/DOTRIACONTANE	82
37.66	DOTRIACONTANE/HEXATRIACONTANE	82

Table S2. Cont.

37.797	PENTADECANE, 6-METHYL-/2,5-DIMETHYL TETRADECANE/5,5-DIMETHYL UNDECANE	83
37.857	DECANE, 3-ETHYL-3-METHYL-	80
37.965	DECANE, 3,3,8-TRIMETHYL	77
38.015	3,8-DECANEDIONE, 2,2,9,9-TETRAMETHYL	66
38.074	SUCCINIC ACID, 2-DECYL OCTADECYL ESTER	74
38.152	DODECYL ETHER	87
38.275	CYCLOHEXANE, 1,1'-(1,3-PROPANEDIYL)BIS-	69
38.405	HEXADECANE/PENTADECANE/EICOSANE	74
38.465	N-((6-(HYDROXYMETHYL)-2- PYRIDYL)METHYL)HEXAMETHYLENIMINE	62
38.525	N-ALLYL-N-ETHYL-2-PROPEN-1-AMINE	73
38.555	SULFUROUS ACID, 2-ETHYLHEXYL OCTADECYL ESTER	83
38.626	DOTRIACONTANE	85
38.716	5,7-DIMETHYLOCTAHYDROCOUMARIN	71
38.77	OXALIC ACID, 2-ISOPROPOXY PHENYL OCTADECYL ESTER	76
38.83	PENTADECANE	64
38.955	TETRAPENTACONTANE/DOTRIACONTANE	81
39.05	PENTATRIACONTANE	73
39.095	PENTADECANE/2,5-DIMETHYL TRIDECANE	83
39.151	TETRATETRACONTANE	78
39.274	TETRAPENTACONTANE	84
39.604	3-HEXEN-1-OL BENZOATE	58
39.869	HEXATRIACONTANE/TETRAPENTACONTANE	83
40.015	1-HEPTACOSANOL	83
40.085	TETRATETRACONTANE	66
40.192	HEXATRIACONTANE/TETRAPENTACONTANE	87
40.28	2,4-DIETHOXY-7-(p-HYDROXYPHENYLCARBOXYL)-8,9- EPOXY-9-(HYDROXYMETHYL)3-OXA-BICYCLO[4.3.0]- CYCLONONANE	84
40.345	TETRATETRACONTANE	71
40.384	DODECANE, 1-BROMO	65
40.504	p-TOLUIC ACID, 4-HEXADECYL ESTER	76
40.568	TETRACOSANE, 2,6,10,15,19,23- HEXAMETHYL/TETRAPENTACONTANE	81
40.62	p-TOLUIC ACID, 2-TETRADECYL ESTER	71
40.723	MALONIC ACID, 2-BUTYL OCTADECYL ESTER	75
40.801	HEXATRIACONTANE DOTRIACONTANE/TETRACONTANE	67
40.886	5-CHLOROVALERIC ACID, PENTADECYL ESTER	68
40.957	5-CHLOROVALERIC ACID, PENTADECYL ESTER	69
41.059	TETRAPENTACONTANE	71
41.388	TETRAPENTACONTANE	87
41.51	FUMARIC ACID, 6-ETHYLOCT-3-YL HEXYL ESTER	66

Table S2. Cont.

41.555	7-METHYLOCTADECANE	62
41.595	CYCLOHEXANE, (1-DECYLUNDECYL)-	68
41.65	UREA, [3-(2-CHLOROPHENYL)-1,4,2-OXATHIAZOL-5-YLIDENE]-	66
41.72	N-[1-(4-PROPYL-4H-1,2,4-TRIAZOL-3-YL)ETHYL]ACETAMIDE	69
41.83	5-CHLOROVALERIC ACID, HEPTADECYL ESTER	70
41.915	TETRAPENTACONTANE	77
42.045	DIMETHYL (1-HYDROXY-1-METHYL-2-PROPENYL)PHOSPHONATE	66
42.087	1H-1,2,3-TRIAZOLO[4,5-D]PYRIMIDINE-5,7(4H,6H)-DIONE	70
42.225	UREA, [3-(2-CHLOROPHENYL)-1,4,2-OXATHIAZOL-5-YLIDENE]-	66
42.267	BENZOIC ACID, NONADECYL ESTER	64
42.455	OXALIC ACID, 2-ISOPROPOXYPHENYL OCTADECYL ESTER	67
42.543	TETRAPENTACONTANE	83
42.57	2,3,4-TRIMETHYLPENTAN-2-OL TETRADECANOATE	63
42.615	(-)-1-PROPYL-2', 6'-DIMETHYL-2-PIPERIDYLCARBOXYANILID	70
43.583	5-METHYL-2-OCTYL-3(2H)-FURANONE	67
43.65	TETRAPENTACONTANE	85
44.219	HENEICOSANE	74
44.728	TETRAPENTACONTANE	84
44.896	SULFUROUS ACID, CYCLOHEXYL METHYL OCTADECYL ESTER	73

(c) Semi-synthetic oil aged at 149 °C.

Retention Time, Min	Compound Name	Percentage Match
33.842	2-OCTYLDODECAN-1-OL	90
34.135	7-OXANONADECANE	85
34.364	1-IODOTETRADECANE	85
34.769	BENZENE, 1-[(1-ETHENYL-5-ETHOXY-2-METHOXY-4-PENTYNYL)OXY] METHYL]-4-METHOXY-	90
36.818	TRITRIACONTANE/PENTATRIACONTANE	86
37.684	DOTRIACONTANE/HEXATRIACONTANE	86
38.186	1,54-DIBROMOTETRAPENTACONTANE	86
38.65	TETRAPENTACONTANE/DOTRIACONTANE	87
39.3	TETRAPENTACONTANE	87
39.901	DOTRIACONTANE /TETRAPENTACONTANE	88
41.438	HEXATRIACONTANE/TETRAPENTACONTANE	86
42.599	DOTRIACONTANE/TETRAPENTACONTANE	87
43.696	TETRAPENTACONTANE	90
44.764	TETRAPENTACONTANE	87

(d) Semi-synthetic oil aged at 200 °C.

Owing to similar fragmentation pattern of linear long chain hydrocarbons, which result in (m/z , Da) 57, 71, 43, 85, 41, 99, 113, 127, 141, 155 as major ions, an ambiguity in identification was observed, especially for tetrapentacontane, dotriacontane, hexatriacontane, tritriacontane, pentatriacontane, hexadecane and tetracosane. These are denoted in the tables in red color font.

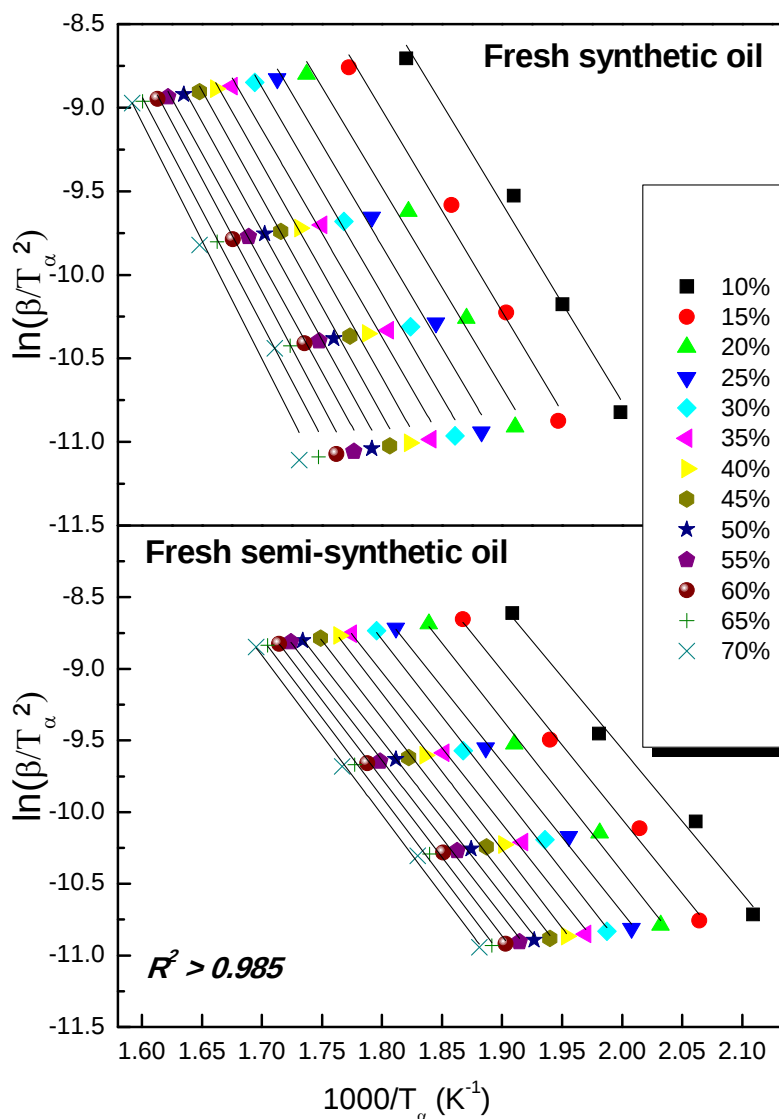


Figure S1. Kissinger-Akahira-Sunose (KAS) plots depicting the linear variation of $\ln(\beta/T_\alpha^2)$ versus $1/T_\alpha$ for different conversions for fresh synthetic and semi-synthetic oils. The conversion range is from 10 wt.% to 70 wt.%. Lines denote straight line fits. The determination coefficients, R^2 , for all the linear fits were greater than 0.985. Similar curves were drawn for the samples aged at different time intervals to evaluate the variation of E_α with conversion.

Table S3. Variation of $T_{\max}$ (in °C) of fresh and oven-aged synthetic and semi-synthetic oils with ageing time. The oil samples were initially subjected to ageing as per standard tests at different temperatures (120, 149 and 200 °C), and the samples collected at different time intervals were subjected to TGA. $T_{\max}$ is evaluated as the temperature at which weight loss rate is maximum. The data corresponds to a sample heating rate of 10 °C min⁻¹ in TGA.

Ageing Time (h) →		(Fresh) 0	6	12	18	24	48	72	96	120	144	168	192	216	240
Synthetic oil	120 °C	304.73	308.33	311.98	310.92	306.98	309.1	307.3	316.45	309.86	312.21	308.78	309.44	313.36	313.34
	149 °C	304.73	304.7	314.73	309.52	307.78	303.15	313.02	311.64	312.38	303.52	306.2			
	200 °C	304.73	308.62	309.61	311.42	312.07	313.24	312.33	312.87	310.65					
Semi- synthetic oil	120 °C	272.41	274.78	274.42	282.91	276.16	276.81	273.91	274.61	272.68	271.61	270.84	267.99	265.9	270.26
	149 °C	272.41	271.81	278.51	275.83	274.04	274.6	271.68	278.73	271.32	273.16	276.69			
	200 °C	272.41	278.76	276.29	279.67	279.17	272.77	278.57	271.68	278.88					