Supplementary information

Cracking of squalene into isoprene as chemical utilization of algae oil

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Experimental methods

1. How to calculate the conversion, selectivity, and yield. The conversion of squalene and the selectivity of the product are calculated from chromatogram obtained by gas chromatograph. Specifically, the conversion of squalene and the product selectivity are determined based on the number of carbons, not on the number of moles as follows:

$$Squalene\ conversion\ (\%) = \left\{1 - \frac{(Molar\ amount\ of\ unreacted\ squalene)}{(Molar\ amount\ of\ squalene)}\right\} \times 100$$

$$Product\ selectivity\ (Carbon\ amount\ basis{:}\%) = \frac{(Molar\ amount\ of\ carbon\ in\ each\ product)}{(Molar\ amount\ of\ carbon\ in\ material)} \times 100$$

$$Yield\ (\%) = (Product\ selectivity\ \times\ Squalene\ conversion)\ \times\ 100$$

We investigated the effect of squalene concentration on the yield and the product distribution by varying the nitrogen and squalene molar ratios of 1:49 – 1:4. However, no significant effect of squalene concentration was observed for the cracking properties of squalene.

2. Chromatogram data. The chromatogram data for the thermal decomposition in the reaction temperature at 873 K and 753 K are shown in Fig. S2 and S3, respectively, as examples of typical chromatogram data. The example of a chromatogram data used for the analysis of the residence time dependence is shown in Fig. S4. A chromatogram of a squalene sample is shown in Fig. S5.

3. Catalysts. In thermal decomposition, quartz sand (Wako Pure Chemical Industries) was set at the catalyst position as an inert catalyst. For the experiments with catalysts, we have used commercial catalysts for MgO (Wako Pure Chemical Industries, Ltd.), TiO_2 (P-25) (Nippon Aerosil), CeO_2 (Daiichi Rare Element Chemical Industry Co., Ltd.), ZrO_2 (Daiichi Rare Element Chemical Industry Co., Ltd.), Al_2O_3 (Catalyzed Chemical Conversion Industry), or ZSM5 (Zeolyst International). On the other hand, the Y_2O_3 catalyst was prepared as follows. Yttrium Nitrate n-Hydrate (0.05 mol / 200 ml) and sodium carbonate (0.05 mol / 200 ml) were mixed. The mixture was dried at 383 K for 17 hours. The dried products were calcined in air at 773 K for 2 hours and then the Y_2O_3 catalyst was obtained. The La_2O_3 catalyst was prepared as follows. Lanthanum nitrate hexahydrate (0.2 mol / 200 mL) and potassium carbonate (0.24 mol / 200 mL) were mixed. The mixture was dried at 383 K for 17 hours. The dried products were calcined in air at 773 K for 2 hours and then the La_2O_3 catalyst was obtained. In every case, the catalysts were filtered to be composed by the particles with size from 355 µm to 600 µm.

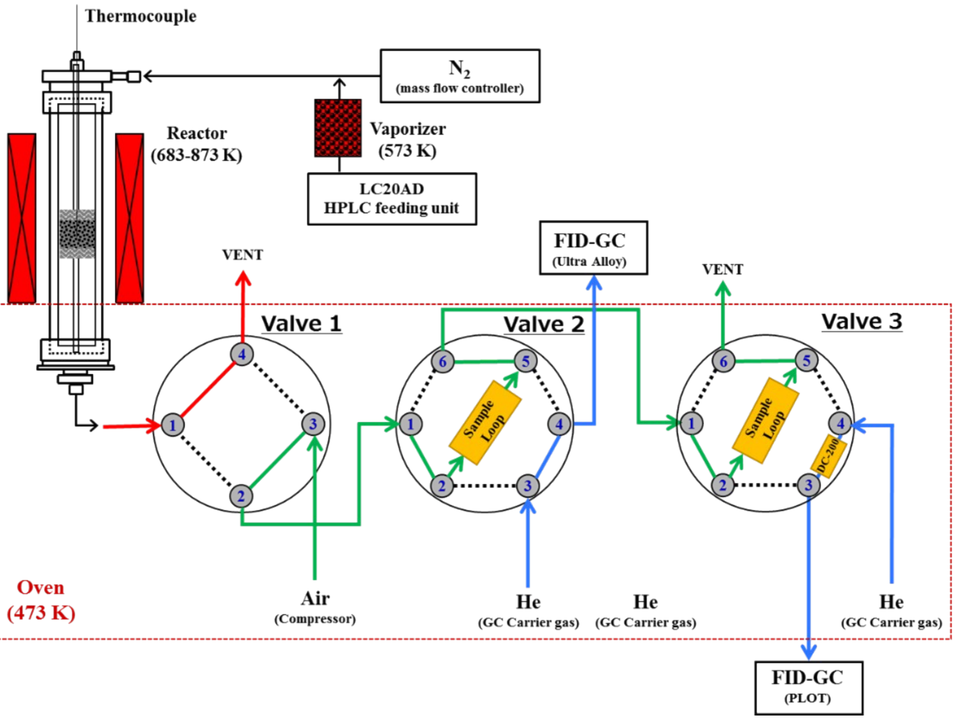


Fig. S1 Schematic diagram of a fix bed flow reactor. The reaction products were analyzed by means of gas chromatogrphs directly connected to the reactor.

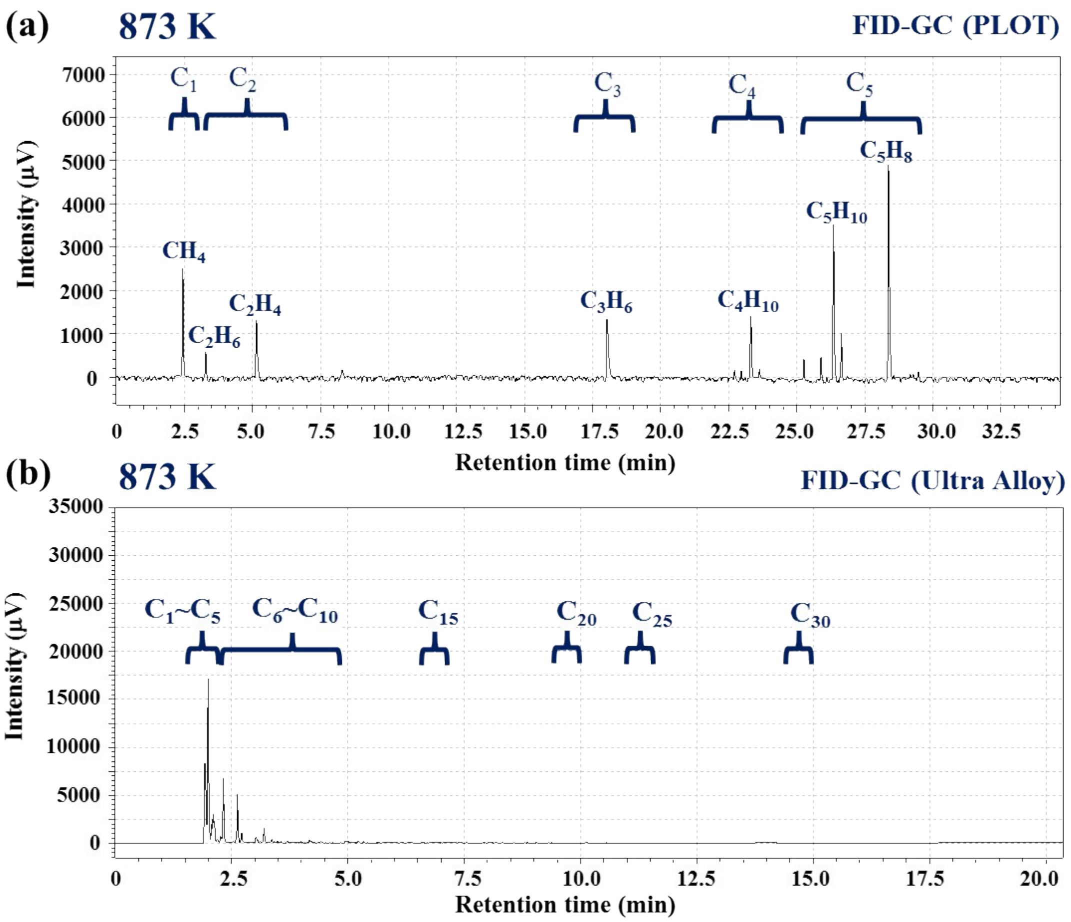


Fig. S2 Squalene thermal decomposition. (a) FID-GC (PLOT), C1-C5, (b) FID-GC (Ultra Alloy), C5-C30, Reaction conditions : Temperature = 873 K, Squalene = 0.70 cc/min, N_2 = 34.4 cc/min, Molar ratio of N_2 by squalene = 49 : 1, Residence time = 0.073 hr/m.

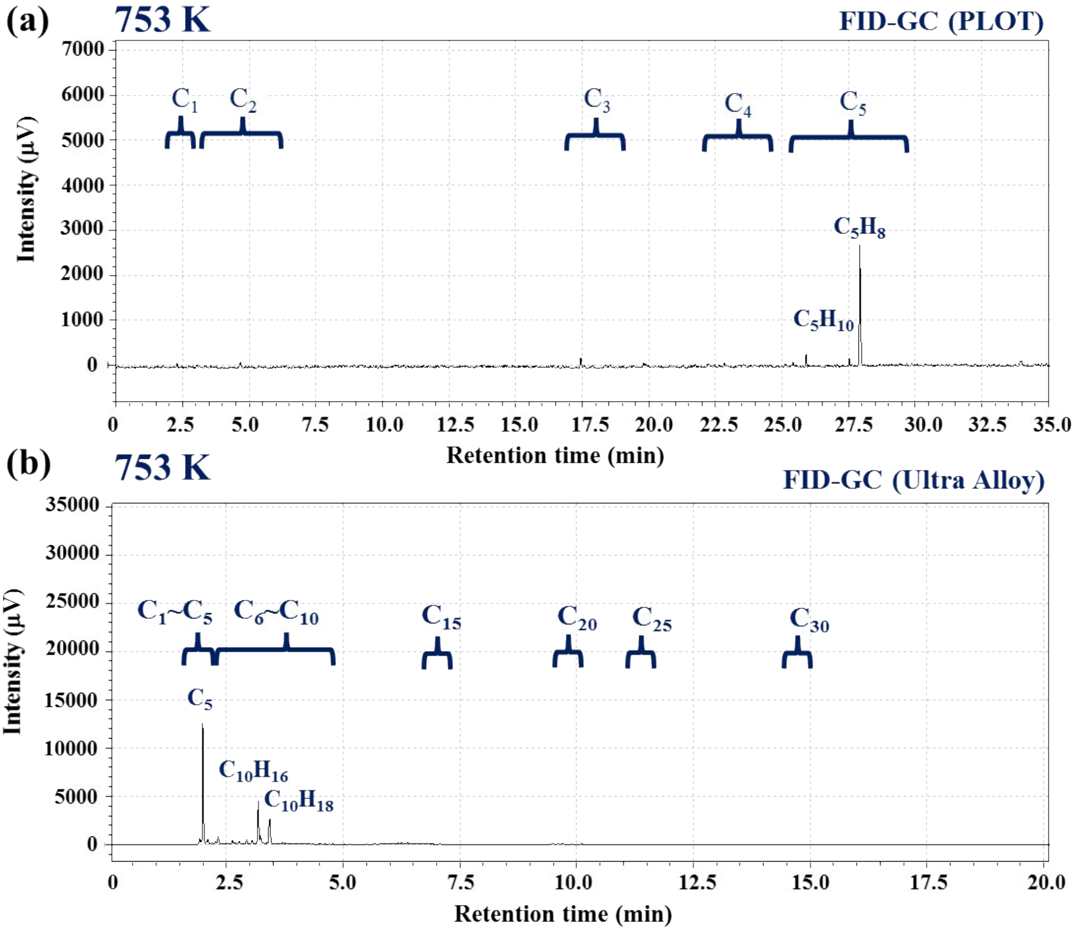


Fig. S3 Squalene thermal decomposition. (a) FID-GC (PLOT), C1-C5, (b) FID-GC (Ultra Alloy), C5-C30, Reaction conditions : Temperature = 753 K, Squalene = 0.70 cc/min, N_2 = 34.4 cc/min, Molar ratio of N_2 by squalene = 49 : 1, Residence time = 0.073 hr/m.

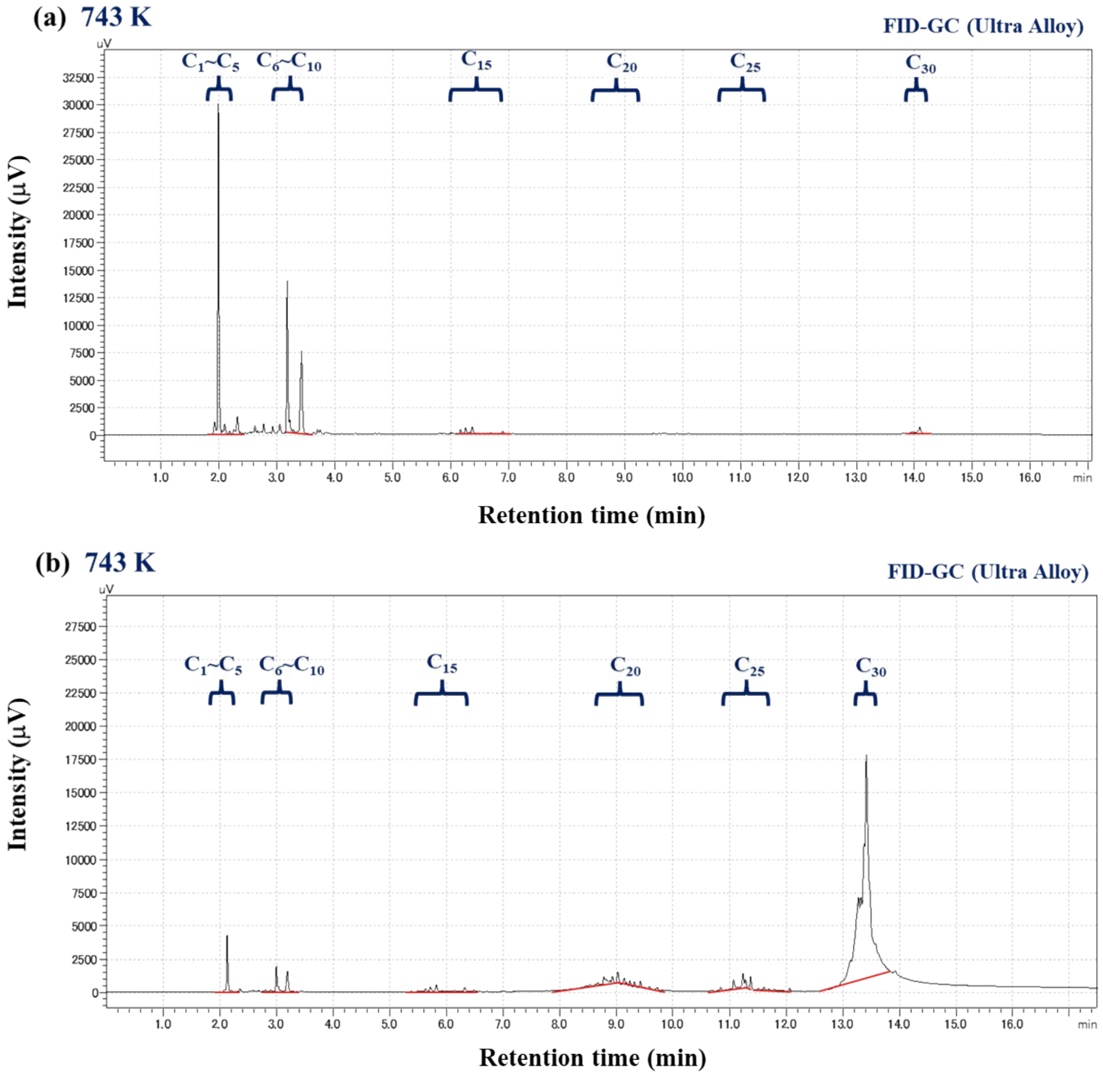


Fig. S4 Effect of products distribution on residence time. (a) FID-GC (Ultra Alloy). Reaction conditions: Temperature = 743 K, Squalene = 0.70 cc/min, N_2 = 34.4 cc/min, Molar ratio of N_2 by squalene = 49 : 1, Residence time = 0.073 hr/m. (b) FID-GC (Ultra Alloy). Reaction conditions: Temperature = 743 K, Squalene = 2.1 cc/min, N_2 = 103.2 cc/min, Molar ratio of N_2 by squalene = 49 : 1, Residence time = 0.024 hr/m. Here we note that the chromatographic peak of squalene after the reaction appears with the shoulder peak at around 13.15 minutes. The intensity of this shoulder peak is very weak in pure squalene. This shoulder peak is considered to be due to an impurity such as an isomer of squalene, which is assumed to increase by the cracking reaction.

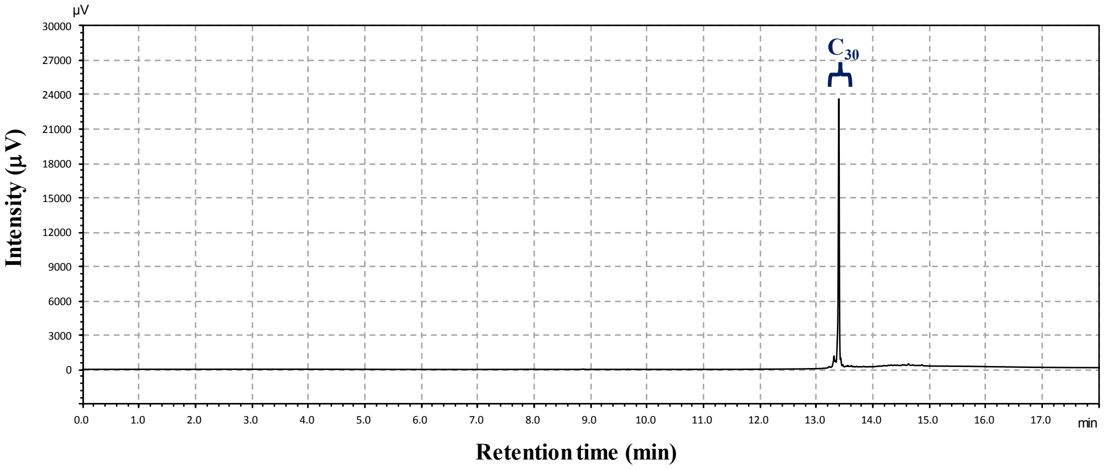
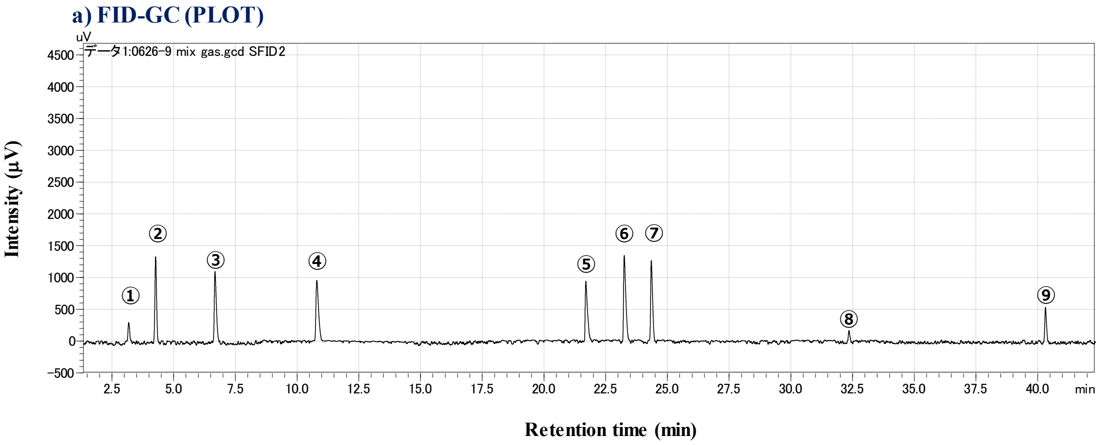
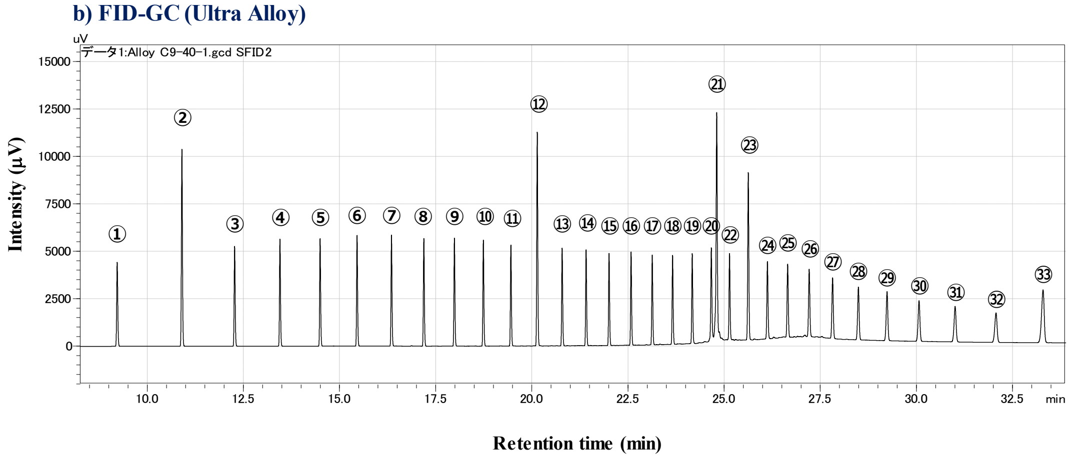


Fig. S5 Squalene peak (FID-GC (Ultra Alloy))



① CH_4 ② C_2H_6 ③ C_2H_4 ④ C_3H_8 ⑤ C_3H_6 ⑥ n-C_4H_{10} ⑦ iso-C_4H_{10} ⑧ C_5H_{12} ⑨ C_5H_8



① C_9H_{20} ② $C_{10}H_{22}$ ③ $C_{11}H_{24}$ ④ $C_{12}H_{26}$ ⑤ $C_{13}H_{28}$ ⑥ $C_{14}H_{30}$ ⑦ $C_{15}H_{32}$ ⑧ $C_{16}H_{34}$ ⑨ $C_{17}H_{36}$ ⑩ $C_{18}H_{38}$
⑪ $C_{19}H_{40}$ ⑫ $C_{20}H_{42}$ ⑬ $C_{21}H_{44}$ ⑭ $C_{22}H_{46}$ ⑮ $C_{23}H_{48}$ ⑯ $C_{24}H_{50}$ ⑰ $C_{25}H_{52}$ ⑱ $C_{26}H_{54}$ ⑲ $C_{27}H_{56}$ ⑳ $C_{28}H_{58}$
㉑ $C_{30}H_{50}$ ㉒ $C_{29}H_{60}$ ㉓ $C_{30}H_{62}$ ㉔ $C_{31}H_{64}$ ㉕ $C_{32}H_{66}$ ㉖ $C_{33}H_{68}$ ㉗ $C_{34}H_{70}$ ㉘ $C_{35}H_{72}$ ㉙ $C_{36}H_{74}$ ㉚ $C_{37}H_{76}$
㉛ $C_{38}H_{78}$ ㉜ $C_{39}H_{80}$ ㉝ $C_{40}H_{82}$

Fig. S6 Results of standard analysis for determination of response factors.

a) C1-C5 for FID-GC (PLOT), Standard gas mixture composed of CH_4, C_2H_6, C_2H_4, C_3H_8, C_3H_6, n -C_4H_{10}, iso-C_4H_{10}, C_5H_{12}, C_5H_8, and N_2 with a molar ratio of 1 : 2 : 2 : 1 : 1 : 1 : 1 : 0.1 : 0.4 : 1.5.

b) C9-C40 for FID-GC (Ultra Alloy), Concentration of each component: C10, C20,and C30 = 5 µg/mL、C40 = 100 µg/mL、others = 50 µg/mL.

Table S1 Relative sensitivity of each component of C1-C5 for FID-GC (PLOT)

Hydrocaron	Molecular weight	Number of moles contained in 10 mL x10^{-5}	Number of carbons contained in 10 ml x10^{-5}	Peak area/number of carbon atoms injected	Relative sensitivity based on carbon number
CH_4	16.04	4.46	4.46	1.00	1.0
C_2H_6	30.07	8.92	17.84	1.15	2.3
C_2H_4	28.05	8.92	17.84	1.00	2.0
C_3H_8	42.08	4.46	13.38	1.06	3.2
n-C_4H_{10}	58.12	4.46	17.84	1.10	4.4
iso-C_4H_{10}	58.12	4.46	17.84	1.05	4.2
C_5H_{12}	72.15	0.45	2.25	1.19	5.9
C_5H_8	68.12	1.79	8.95	1.00	5.0

Standard gas mixture composed of CH_4, C_2H_6, C_2H_4, C_3H_8, C_3H_6, n -C_4H_{10}, iso-C_4H_{10}, C_5H_{12}, C_5H_8, and N_2 with a molar ratio of 1 : 2 : 2 : 1 : 1 : 1 : 1 : 0.1 : 0.4 : 1.5.

Table S2 Relative sensitivity of each component of C9-C40 for FID-GC (Ultra Alloy)

Hydrocaron	Molecular weight	Number of moles contained in 10 mL x10^{-7}	Number of carbons contained in 10 ml x10^{-7}	Peak area/number of carbon atoms injected	Relative sensitivity based on carbon number
n-Nonane	128.25	3.90	35.1	1.0	9.0
n-Decane	142.28	1.76	17.6	1.0	10.0
n-Undecane	156.31	3.20	35.2	1.0	11.0
n-Dodecane	170.34	2.94	35.2	1.0	12.0
n-tridecane	184.37	2.71	35.3	1.0	13.0
n-Tetradecane	198.39	2.52	35.3	1.0	14.0
n-Pentadecane	212.41	2.35	35.3	1.0	15.0
n-Hxadecane	226.44	2.21	35.3	1.0	16.0
n-Heptadecane	240.47	2.08	35.3	1.0	17.0
n-Octadecane	254.49	1.96	35.4	1.0	18.0
n-Nonadecane	268.52	1.86	35.4	1.0	19.0
n-Elocosane	282.55	1.77	35.4	1.0	20.0
n-Henelcosane	296.58	0.84	17.7	1.0	21.0
n-Docsane	310.60	1.61	35.4	1.0	22.0
n-Tricosane	324.63	1.54	35.4	1.0	23.0
n-Teracosane	338.65	1.48	35.4	1.0	24.0
n-Pentacosane	352.69	1.42	35.4	1.0	25.0
n-Hexacosane	366.71	1.36	35.5	1.0	26.0
n-Heptacosane	380.74	1.31	35.5	1.0	27.0
n-Octacosane	394.77	1.27	35.5	1.0	28.0
Squalene	410.73	0.61	17.7	1.0	30.0
n-Nonacosane	408.79	1.22	36.7	1.0	29.0
n-Triacotane	422.82	0.59	18.3	1.0	30.0
n-Hentriacontane	436.85	1.14	36.6	1.0	31.0
n-Dotriacontane	450.88	1.11	36.6	1.0	32.0
n-Tritriacontane	464.90	1.08	36.6	1.0	33.0
n-Teratriacontane	478.93	1.04	36.5	1.0	34.0
n-Pentatriaconatne	492.96	1.01	36.5	1.0	35.0
n-Hexatriaconatane	506.97	0.99	36.5	1.0	36.0
n-Heptatriaconatene	521.00	0.96	36.5	1.0	37.0
n-Octatriacontane	535.03	0.93	36.4	1.0	38.0
n-Nonatriacontane	549.05	0.91	36.4	1.0	39.0
n-Tertacontane	563.08	1.78	71.0	1.0	40.0

Concentration of each component: C10, C20,and C30 = 5 µg/ mL, C40 = 100 µg/mL, others = 50 µg/mL.

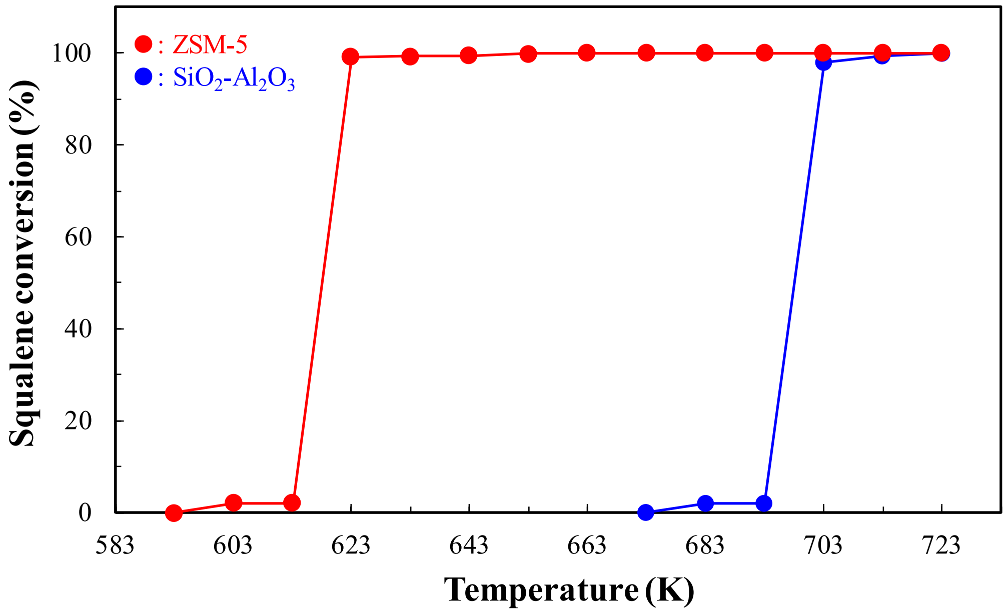


Fig. S7 (a)-(b) Effect of acid catalysts on squalene conversion at various temperature. Condition: catalyst, 1.0 g; squalene (gas), 0.70 cc/min ; N_2, 34.4 cc/min; Molar ratio of N2 by squalene = 49 : 1; liner velocity, 13.7 m/hr (residence time, 0.073 hr/m).