Electronic supplementary materials *Mendeleev Commun.*, 2026, **36**, 317–319

Formation of high-octane motor fuel *via* liquid phase alkylation promoted by new H_2SO_4–alkane Winsor III microemulsion systems

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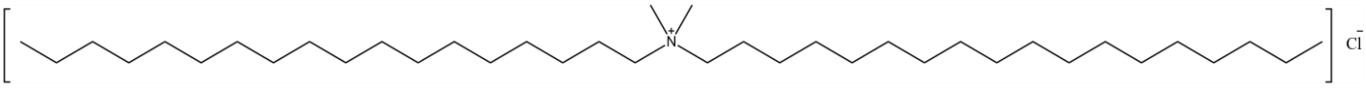
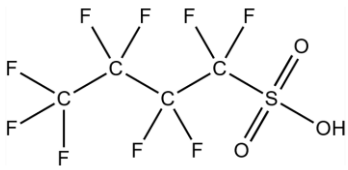
Chemicals

All reagents are commercially available.

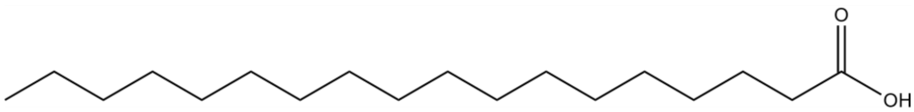
- DimethylDioctadecylAmmonium Chloride (DODMAC) $[CH_3(CH_2)_{17}]_2[CH_3]_2N^+Cl^-$ – SigmaAldrich.com, ≥ 97%.



- Nonanfluorobutane sulfonic acid (NFBSA) $CF_3(CF_2)_3SO_3H$ – SigmaAldrich.com, ≥ 97%.



- Stearic acid (StA) $CH_3(CH_2)_{16}COOH$ – SigmaAldrich.com, ≥ 97% (AT).



- 1-butene ($C4^=$) – SigmaAldrich, ≥ 99.6%.
- Sulfuric acid (SA) – Acros Organic, 96%.
- Isobutane (iB) – SigmaAldrich, 99+%.
- Isopentane (iP) – SigmaAldrich 99+%.

Experimental procedure for alkylation experiments with i-butane

Alkylation experiments are performed in a stainless-steel stirred laboratory reactor (100 ml volume) with pitched blade turbine. Stirring velocity may be varied from ~ 500 to 2800 rpm. Reactor is equipped with cooling jacket and being cooled during experiments with help of refrigerated circulator. Only chemically stable and solvent resistant Viton gaskets / sealings / tubes are used.

Experimental procedure is as follows.

All actions with chemicals are carried out in extra dry atmosphere. A dehumidified experimental box is used for any manipulations with reagents and open cold reactor.

Before experiments reactor is very carefully dried including magnet drive internals. Before experiments with pure SA all parts of reactor are cleaned from DODMAC traces with chloroform, then washed and carefully dried.

The weight of reactor is measured with help of a mass balance Sinko Denshi CJ-8200ER with precision 0.1 g.

Before experiment the surfactants are dissolved in H_2SO_4 with help of heating (~50°C) followed by obtained solution loading into reactor with subsequent sealing of the reactor and leakage-proof testing.

The weight of reactor is measured (actual **m(H_2SO_4)** is obtained).

With help of syringe pump (ISCO Model 500D and 250D are used) the small portion of iB is added into reactor followed by the opening of one of reactor gas valve for removing of iB vapor. Action is repeated to completely remove the rest of air from the reactor. Then required iB quantity is introduced.

The weight of the reactor is measured (actual **m(iB)** is obtained).

SA/iB/Surfactant system is stirred to make emulsion for 30 min.

Reactor is cooled to operating T while keeping it stirred.

1-butene ($C4^{=}$) injection is started using a mass flow controller. ($C4^{=}$ saturated vapor pressure in the $C4^{=}$ cylinder must be sufficiently higher than the iB saturated vapor pressure inside the reactor at reaction T, so elevated T for $C4^{=}$ is needed inside syringe pump).

It is important to introduce $C4^{=}$ uniformly while dispersing it as fast as possible, avoiding any $C4^{=}$ local concentration increasing, to get the best results. $C4^{=}$ is introduced through a MasterFlex Viton tube with thin inner channel 0.5 mm diameter directly to the impeller area. Viton tube is connected to a valve, which, in turn, is connected to the $C4^{=}$ line. The dead volume of this system (tube + valve) is approximately 0.15 ml volume <=> 3% of total introduced liquid butene (total amount 2.8 g).

After stopping of $C4^{=}$ injection the valve connected to injection tube is closed, then the valve is heated to remove the rest of $C4^{=}$ from channel into the reaction volume.

After ending of the $C4^{=}$ addition process (appr. it takes 20 min at SV =0.3 h^{-1}+ 5 min for removing $C4^{=}$ from tube) the reactor is left to be stirred for 1h. It is needed to be sure we obtain equilibrium distribution of reaction products inside reaction mixture.

Reactor cooling jacket is purged by the dry air flow to get rid it of any traces of coolant (water + byt-alcohol mixture).

The weight of the reactor is measured (it is needed to control the mass of $C4^{=}$ **m($C4^{=}$)** introduced and absence of any leakage).

Reactor is cooled again. iB is started to be removed by very little opening of a gas valve of the reactor. Gas after the valve additionally passes through a glass cold trap cooled at -15°C to prevent alkylate carrying away. Exit of the gas line is connected to GC to control the gas composition online (one gas phase analysis per appr. 40 min). Passing gas after the cold trap contains mainly iB, but the flow also includes various components, which relative concentrations are different from that in alkylate. It has been found also that isooctanes isomers evaporates better into the gas phase than dimethyhexanes, resulting in the decreasing of the calculated ONs if analysis of gas phase is not included into calculation.

After iB is stopped to be released itself, the reactor is heated appr. to 10°C followed by extra dry air bubbling through the reaction mixture (at the lowest reachable flow rate) and gentle stirring. It is needed to remove as much iB as possible. Total time for iB removal during these two stages is about 5-6 h in case of system modified by DODMAC. After iB removal the reactor's cooling jacket is purged by dry air flow and the weights of the reactor and the cold trap content are measured providing the mass of gas removed and the masses of organic phases in the reactor as well as in the cold trap. After averaging of iB concentration values in all gaseous samples the mass of carried away alkylate is estimated (only few %). Adding this value to the masses of alkylate stayed in the reactor and entrapped by the cold trap provides the total mass **m(0)** of alkylate phase, which is used then to calculate yield and selectivity.

The content of the cold trap is mixed with organic phase in the reactor. The content of the reactor is kept in a leak-tight glass bottle at -20°C. After separation of organic phase, the sample is taken for GC analysis. Lab centrifuge may be also successfully used to separate phases efficiently.

Experimental procedure for alkylation experiments with i-pentane

Surfactants are dissolved in H_2SO_4 with help of heating (~50°C) followed by solution cooling. H_2SO_4 and iP are loaded into the reactor with help of peristaltic MasterFlex pump and the reactor is kept stirred for 30 minutes and only then 1-butene ($C4^=$) injection is started using a mass flow controller. All masses are controlled with help of a mass balance Sinko Denshi CJ-8200ER with precision 0.1 g by direct measurement of the reactor weights like it is described above.

Some excess pressure of nitrogen (~ 0.4 bar) is retained to make it possible the reaction mixture sampling without the reactor opening. After reaction completion and waiting for phases separation (appr. 0.5 hour) a sample of separated alkylate is taken for GC analysis. Samples of reaction mixture are kept in a freezer.

Completion of the alkylation reaction under different conditions is verified by GC analysis of alkylate on 1-butene and 2-butene. During experiment the degree of olefin conversion and the reaction rate may be also roughly controlled by reading the pressure value inside the reactor, which gives the amount of olefin still persisted in the gas phase. In the case of DODMAC surfactant added olefin is consumed by the reaction mixture very fast and reacts immediately.

Procedure for alkylation experiments with ASO modified H_2SO_4

Side reactions with H_2SO_4 proceed as formation of alkyl-sulfates. Oligomerization and side reactions of olefins with carbonium ions happen, with the main by-product sometimes referred to as “acid soluble oils” (ASO) produced and accumulated in the H_2SO_4 phase. Well-known, that industrial process operates only if a sufficient ASO amount is presented in H_2SO_4, serving as a surfactant [S1]. Keeping the balance between ASO content, mixing efficiency, reaction heat removal, strength of H_2SO_4 and the reaction performance are the keys to success for SAAU. Importantly, that H_2SO_4 also acts as reaction heat sink and heat transfer agent.

For our experiments the synthetic ASO was produced by addition of 2.8 g of 1-butene into 160 g of H_2SO_4 and several days aging at -20°C. Such formulation leads to the best results in alkylation reaction. Repeated usage of such ASO modified H_2SO_4 has been also studied. Comparison also has been made with DODMAC modified H_2SO_4 containing synthetic ASO. It is worth to note, that 2.8 grams of $C4^=$ in 160 grams in H_2SO_4 is equivalent to $(4/2)*(2.8/29)/(160/98) \approx 1/8$ ratio between amount of “organic” protons to total H_2SO_4 protons. For DODMAC + pure H_2SO_4 system the same ratio is about 1/1000, 100 times smaller. We may expect hence, that dozens of times alkylation runs with DODMAC are needed to produce such amount of ASO.

Repeated usage of ASO+ H_2SO_4 system has been also studied (9 reuses). Finally, after some decreasing in alkylate quality, DODMAC was added into this system. Despite a lot of by-products formed inside H_2SO_4, DODMAC presence makes results better again (ONs).

Calculation of alkylation reaction parameters

Based on the chromatographic analysis data, the main parameters of the alkylation reaction are calculated, including the composition of the true alkylate by excluding the remains of isobutane and other by-product hydrocarbons with a chain length of less than 6 (as a rule, the amount of the latter was less than 1 mass %).

The following values are used to describe the alkylation reaction for iso-butane alkylation (the similar for iso-pentane):

- Space velocity of olefin feeding (h^{-1}): $SV = \frac{\text{Volume flow rate of olefin}}{\text{V}(\text{H}_2\text{SO}_4)}$;
- Initial iso-alkane/olefin ratio (mol/mol) (iB/O);

- Reacted iso-alkane/olefin ratio (mol/mol): $R_{iB/O}$;
- Yield of all C8 isomers (for C4⁼) per 1 mole of C4⁼, including self-alkylation route (mol/mol): $Y_{O\rightarrow \mathrm{C8}}$;
- Yield of trimethylpentanes per 1 mole of C4⁼ or iB (mol/mol): $Y_{O\rightarrow \mathrm{TMP}}$, $Y_{iB\rightarrow \mathrm{TMP}}$;
- Yield of isomers C8 per 1 mole of iB (mol/mol): $Y_{iB\rightarrow \mathrm{C8}}$;
- True alkylate – the sum of all C6+ products in the reaction mixture after reaction completion;
- Mass yield of alkylate: $Y_{m_A/m_O} = \left(\sum_{i=6}^{10+} m(Ci)\right)/(m\ of\ olefin)$;
- Mass yield of all C8: $Y_{m_{C8}/m_O} = \left(m(C8)\right)/(m\ of\ olefin)$;
- Volume yield of alkylate: $Y_{V_A/V_O} = \left(\sum_{i=6}^{12} \frac{m(Ci)}{\rho(Ci)}\right) / \left(\frac{m(olefin)}{\rho(liq.olefin)}\right)$;
- Volume yield of all C8: $Y_{V_{C9}/V_O} = \left(\frac{m(C8)}{\rho(C8)}\right) / \left(\frac{m(olefin)}{\rho(liq.olefin)}\right)$;
- Selectivity for C8: $S_{\mathrm{C8}} = n(\mathrm{C8})/\sum_{x=C6}^{C12+} n(x)$, *n* – moles of substance.
- Mole ratio of trimethylpentanes to dimethylhexanes TMP/DMH.

Octane numbers are estimated using GC analysis results as described [S2].

Table S1 – Various lumps with of RON and MON values to calculate octane number of alkylate.

	RON	MON	density, g/ml
nButane	94.0	89.6	0.573
nPentane	62.0	62.6	0.621
nHexane	24.8	26.0	0.656
nHeptane	0.0	0.0	0.682
nOctane	-15.0	-20.0	0.699
nNonane	-20.0	-20.0	0.715
nDecane	-30.0	-30.0	0.728
nUndecane	-35.0	-35.0	0.737
nDodecane	-40.0	-40.0	0.745
isoButane	102.0	97.6	0.552
isoPentane	92.0	90.3	0.616
C6-MonoMethyls	76.0	73.9	0.654
2,2-DiMethylButane	91.8	93.4	0.644
2,3-DiMethylButane	105.8	94.3	0.658
C7-MonoMethyls	52.0	52.0	0.679
C7-DiMethyls	93.8	90.0	0.680
2,2,3-TriMethylButane	112.8	101.3	0.687
C8-MonoMethyls	25.0	32.3	0.704
C8-DiMethyls	69.0	74.5	0.701
C8-TriMethyls	105.0	98.8	0.710
C9-MonoMethyls	15.0	23.3	0.714
C9-DiMethyls	50.0	60.0	0.716
C9-TriMethyls	100.0	93.0	0.724
C10-MonoMethyls	10.0	10.0	0.727
C10-DiMethyls	40.0	40.0	0.730
C10-TriMethyls	95.0	87.0	0.737
C11-MonoMethyls	5.0	5.0	0.740
C11-DiMethyls	35.0	35.0	0.740
C11-TriMethyls	90.0	82.0	0.740
C12-MonoMethyls	5.0	5.0	0.750
C12-DiMethyls	30.0	30.0	0.750
C12-TriMethyls	85.0	80.0	0.750

NMR studies

NMR techniques are used for analyzing the composition of reaction mixture and sulfuric acid phase, studying of surfactants stability and solubility, Winsor type III microemulsion initial structural studying.

^1H and ^{13}C NMR spectra have been recorded on Bruker AVANCE-400 spectrometer at 400.13 and 100.61 MHz respectively at different temperatures. Spectral assignments are based on ^1H-^1H correlations provided by COSY, COSY Long Range and NOESY 2D spectra and ^1H-^{13}C 2D correlations through one-bond and multiple-bonds connections. Standard DEPT90 and DEPT135 experiments have been used for spectral editing. Quantitative ^{13}C NMR spectra have been recorded using inverse gated decoupling. $^1J_{CH}$ coupling constants have been estimated by fitting of normal gated decoupled spectra.

Sulfuric acid phase has been studied by NMR ^1H technique to determine the content of organic compounds residues (ASO - acid soluble oil) as follows. Organic phase is separated with help of a separating funnel followed by double extraction with $CDCl_3$ to remove the residual alkylate and surfactant from the acid phase. It is checked in a separate experiment that surfactant is readily dissolved into $CDCl_3$ and don't influent on NMR analysis of H_2SO_4 phase. All signals of organic protons are integrated and compared with sums of signals of H_2SO_4 protons.

NMR data for DODMAC are represented on figures S1 and S2. ^{13}C NMR signals of DODMAC in $CDCl_3$ (δ, ppm): 63.47 (C1), 51.25 (NMe), 31.87 (C16), 29.66-29.64 (five C atoms), 29.61 (two C atoms, including C14), 29.57 (C7), 29.45 (C6), 29.35 (C5), 29.31 (C15), 29.18 (C4), 26.25 (C3), 22.71 (C2), 22.63 (C17), 14.06 (C18).

It is found that DODMAC is insoluble neither conc. H_2SO_4 (less than 0.04 g/100 ml at 23°C) or alkylate.

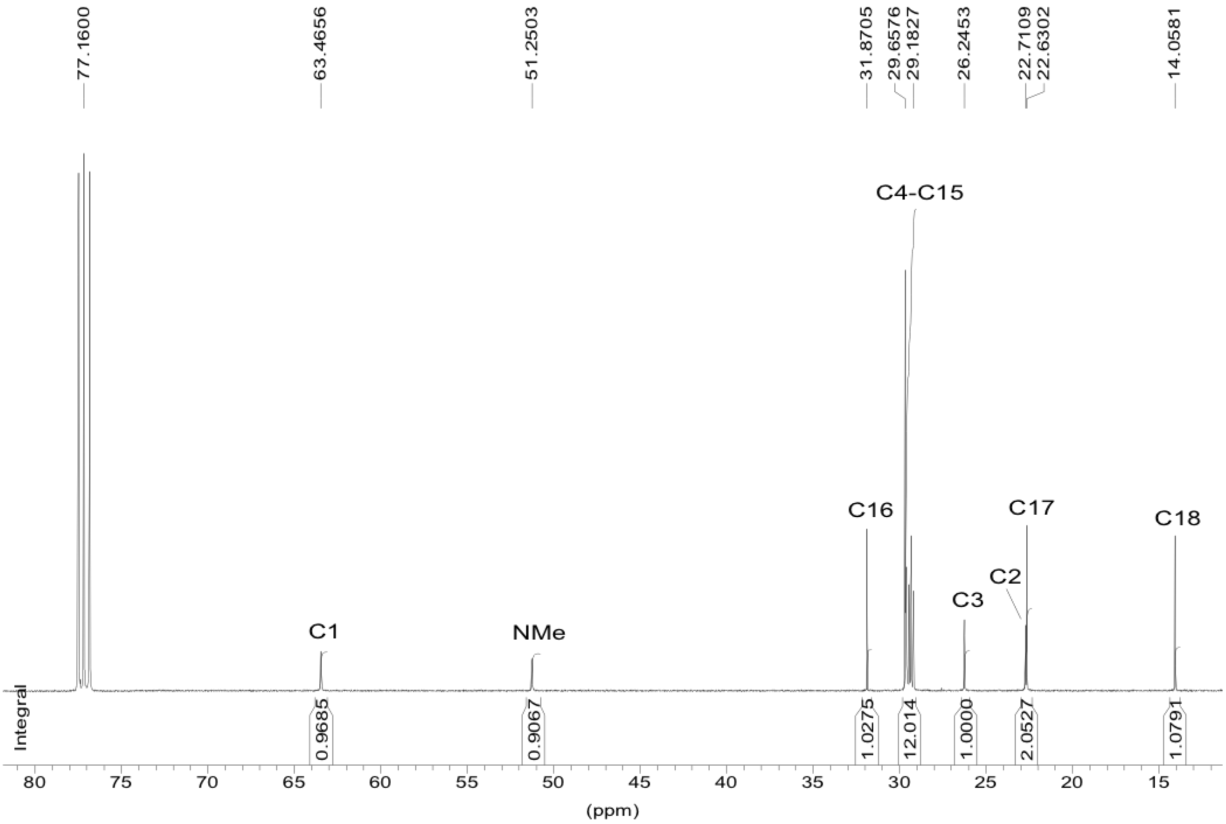


Figure S1 The quantitative (INVGATE, delay 60 s) ^{13}C NMR spectrum of DODMAC solution in $CDCl_3$. The long chain ^{13}C NMR signals are labeled from N-CH_2 (C1) to CH_3 (C18). Methyl groups were assigned by DEPT135. Where possible, a few signals were assigned by 2D ^{13}C-^1H correlation spectroscopy using data from 2D 1H-1H COSY spectra.

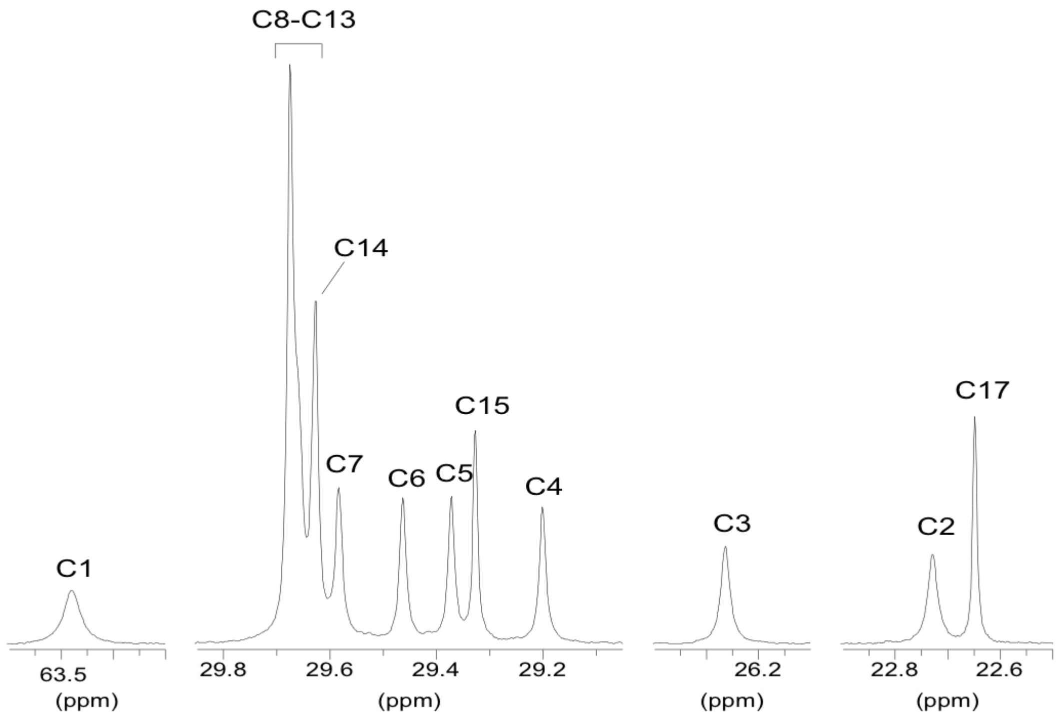


Figure S2 Expansions of suitable regions of the quantitative (INVGATE, delay 60 s) ^{13}C NMR spectrum of DODMAC solution in $CDCl_3$. Vertical and horizontal scale is the same for all plotted regions. Height of a signal is inversely proportional to its width.

The solubility of NFBSA in conc. H_2SO_4 revealed that the specified surfactant exhibits good solubility (virtually unlimited). The investigation has been conducted by comparing the NMR signals of a sample of pure conc. H_2SO_4 to which the surfactant was gradually added. Figure S3 shows the ^{13}C NMR spectrum of the solution of NFBSA in conc. H_2SO_4: C4 (CF_3) δ 116.86 $^1J_{CF}$=288 Hz, $^2J_{CF}$=33 Hz; C3 (CF_2) δ 108.22 $^1J_{CF}$=270 Hz, $^2J_{CF}$=40 Hz (q), 33 Hz (t); C2 (CF_2) δ 109.85 $^1J_{CF}$=269 Hz, $^2J_{CF}$=32 Hz; C1 (CF_2SO_3H) δ 113.24 $^1J_{CF}$=295 Hz, $^2J_{CF}$=35 Hz.

Figure S4 presents a comparison of the ^{13}C NMR spectra of NFBSA in sulfuric acid and in the middle phase of the H_2SO_4-(NFBSA+StA)-nC6 system.

Figure S5 shows the ^{13}C spectrum of the middle phase of the H_2SO_4-(NFBSA+StA)-nC6 system. The signal of the carboxyl group of StA is located around 193 ppm and is significantly moved to higher chemical shifts compared to solutions in common organic solvents (180.62 ppm for the solution of StA in $CDCl_3$). A similar shift is observed for solutions of lower homologs of carboxylic acids in conc. H_2SO_4 and superacids, which is explained by the protonation of the carboxyl group by strong acids, with respect to which StA acts as a base.

All used surfactant systems are chemically stable in contact with concentrated H_2SO_4, that has been proved by NMR, for the time period 5 days.

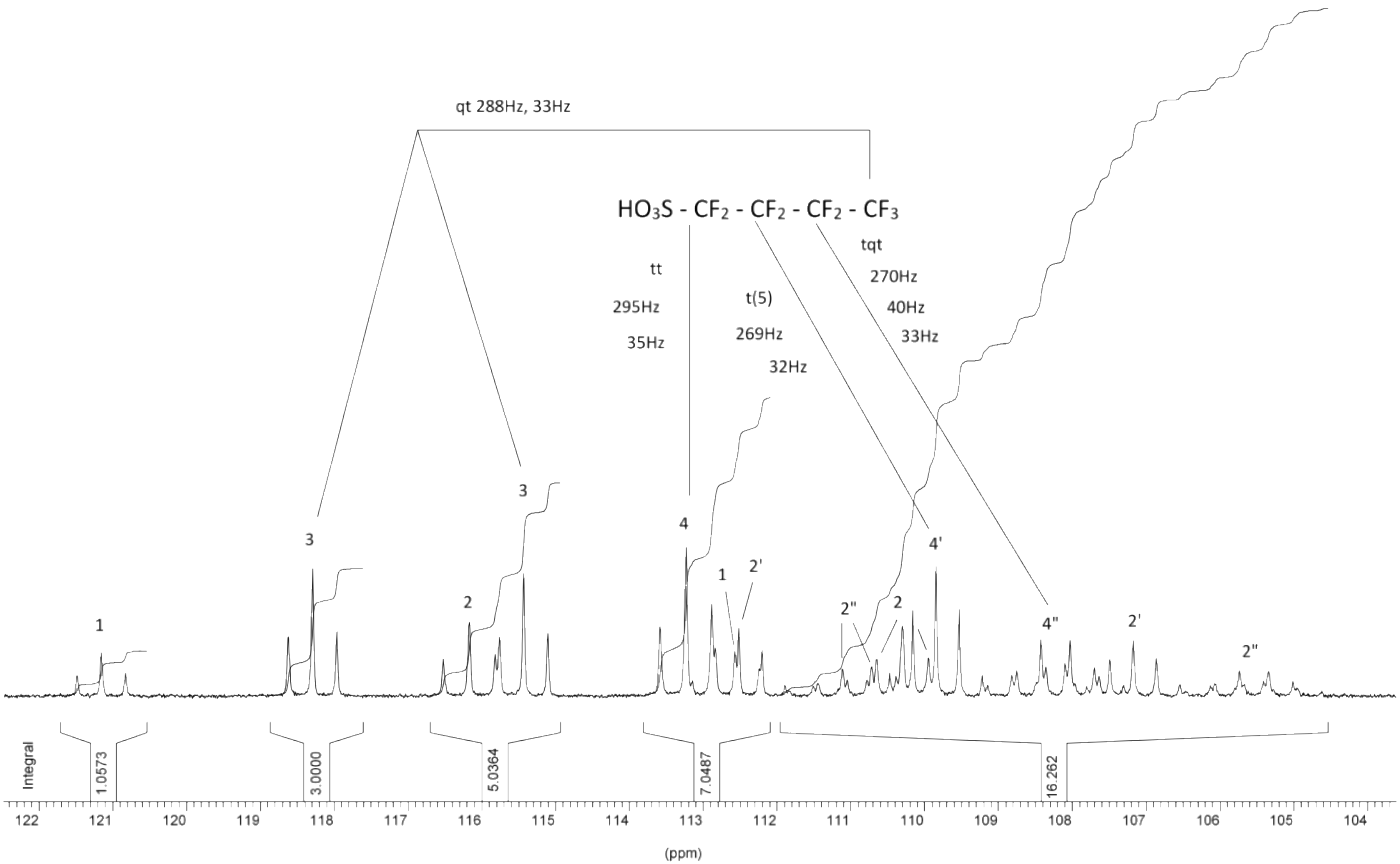


Figure S3 [13]C NMR spectrum of the $C_4F_9SO_3H$ solution in H_2SO_4. (qt – quartet of triplets, tt – triplet of triplets, t(5) – triplet of quintets, tqt – triplet of quartets of triplets).

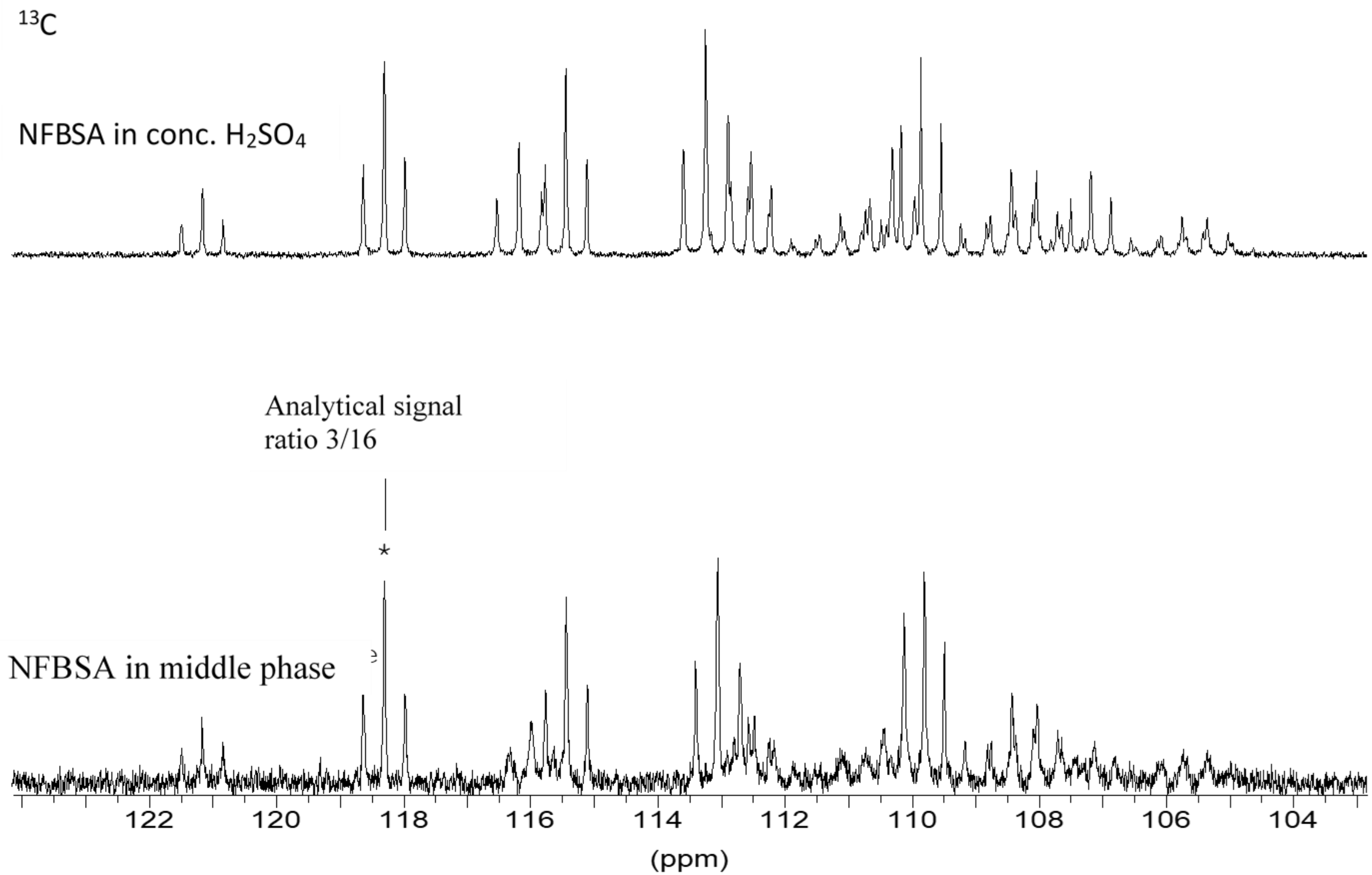


Figure S4 ^{13}C NMR spectra of NFBSA in sulfuric acid and in the middle phase of the H_2SO_4-(NFBSA+StA)-nC6 system.

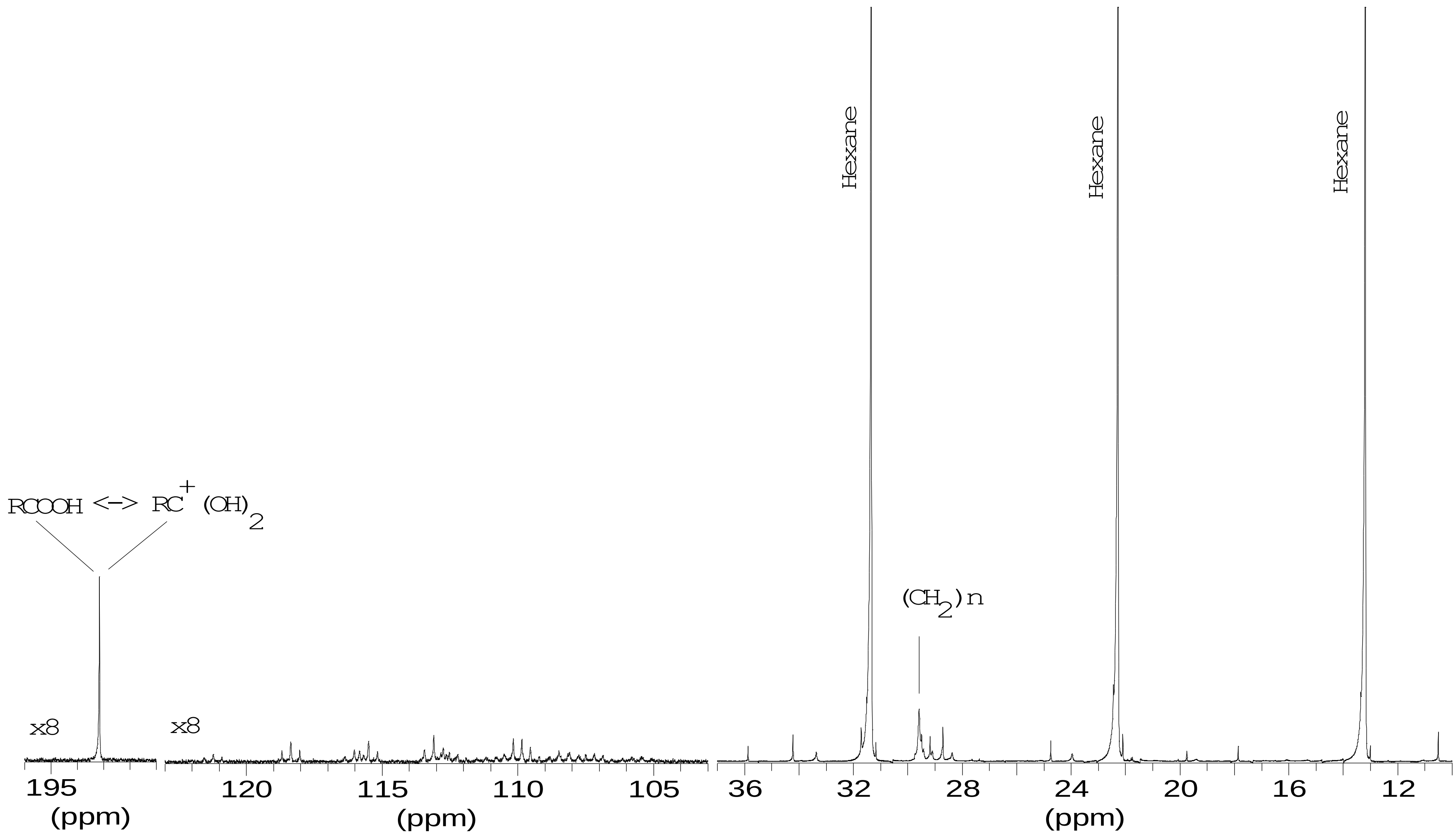


Figure S5 ^{13}C NMR middle phase spectrum of the H_2SO_4-(NFBSA+StA)-nC6 system.

Microemulsions formation and basic reaction pathways

Figure S6 represents the basic pathways for sulfuric acid alkylation reaction with presence and absence of surfactants capable to form Winsor III microemulsion. Figure S7 shows how microemulsions formed look like.

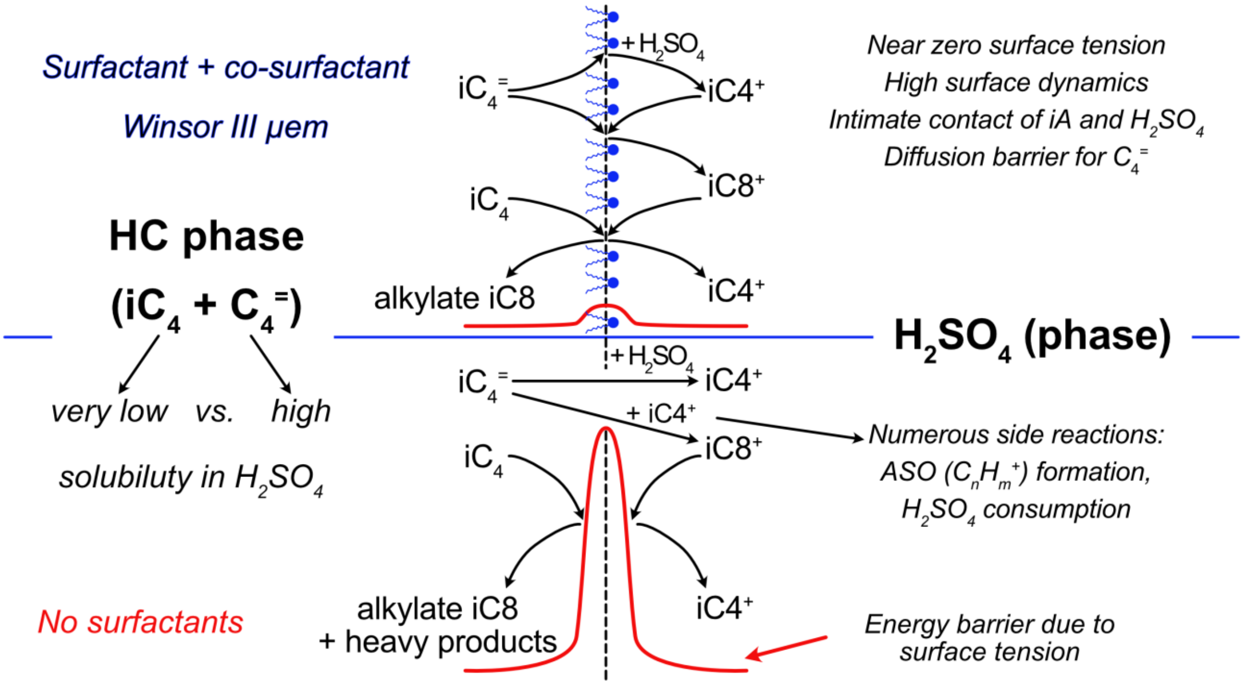


Figure S6 Motor fuel alkylation reaction catalyzed by H_2SO_4 – the basic reaction pathways with and without the presence of surfactants forming WIII μem.

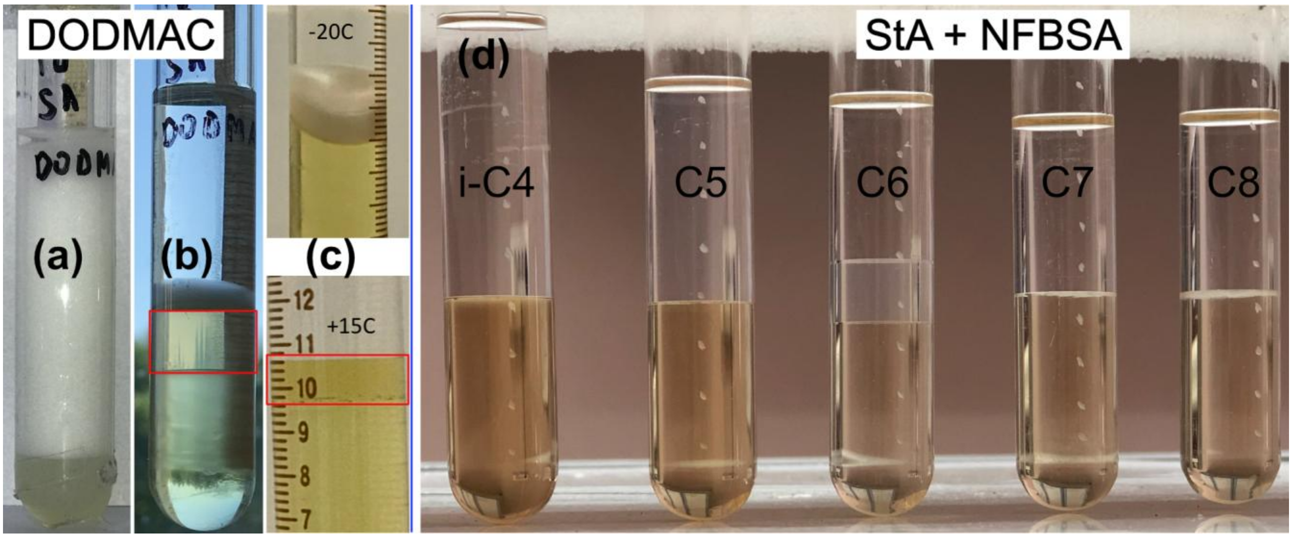


Figure S7 Winsor III type μems: DODMAC (a-c) and StA+NFBSA (d) modified H_2SO_4 / alkanes systems with middle phase formation. (a) – initial emulsion and (b) – after separation of DODMAC + iC4 at +15°C; (c) – DODMAC + n-C6 at +15°C and -20°C; (d) – StA+NFBSA + i-C4 or n-C5/C8 alkanes at +15°C. For the StA+NFBSA μem the WIII found is close to be a balanced μem.

Alkylation reaction iC4 or iC5 + 1-butene ($C4^{=}$) results

Table S2 Alkylation reaction iC4 or iC5 + $C4^{=}$ results with 100% conversion of $C4^{=}$: yield (Y), selectivity to C8/C9 (S), ratio of iA/$C4^{=}$ reacted, ONs, C8 or C9 content in “true” alkylate (only C6+ compounds). $V(H_2SO_4)/V(iA)=1$

Sample	1[a]	2[a]	3[a,]	4[a]	5[b]	6[b]	7[b]	8[b]	9[b]	10[b]	11[b]
Alkylation system	iC4 + $C4^{=}$ (mole ratio 7.7/1)								iC5 + $C4^{=}$ (mole ratio 7/1)		
Surfactant system	StA + NFBSA			Pure H_2SO_4	Pure H_2SO_4		DODMAC	ASO[c]	DODMAC		
Surfactant w.%	0.03/0.09	0.03/0	0.03/0.09	–	–	–	0.03	0	0.03	0	0
T, °C	5	5	20	5	2	2	2	2	5	5	5
rpm	750	750	750	750	750	1500	750	750	750	750	2800
SV, h^{-1}	$C4^{=}$ was preliminary added into iC4				0.3	0.3	0.3	0.3	0.3	0.3	0.3
Y, mol C8 or C9/mol $C4^{=}$	1.216	0.848	0.723	0.449	0.341	0.682	1.436	0.912	0.886	0.31	0.623
Y[d], vol alkylate/vol $C4^{=}$	2.6	1.4	2.0	1.4	1.5	2.1	2.8	2.0	2.7	1.9	2.5
Ratio *iC4/* $C4^{=}$ reacted	1.9	0.64	1.3	0.6	0.9	1.9	2.5	1.8	2	1.2	1.7
S, % $C4^{=}$-> C8/C9	87	66	76	67	45	63	91	82	62	36	52
RON[d]	99	98.1	94	93.1	88.9	93.4	100.1	97.8	92.5	85	90
MON	93.9	93.1	89	88.4	84.4	88.7	94.9	92.9	86.5	81	85
C8 (for iC4) / C9 (iC5) in true alkylate, wt.%	85	81.7	68	57	39.9	58.6	89.6	79.4	63	33	50
C12+ in true alkylate, wt.%	1.8	2.4	4.7	10.2	17	8	1.5	3	3	14	7

[a] 1b is preliminary added to i-alkane. [b] 1b is injected to i-alkane with space velocity SV=0.3 h^{-1}. [c] Synthetic ASO addition, ASO has been prepared by addition of 2.8 g of 1b into 160 g of H_2SO_4 and several days aging at 20°C.
[d] Typical values for the SAAU: Y=1.8 vol/vol, RON=93÷95.

Formation of acid soluble oils (ASO)

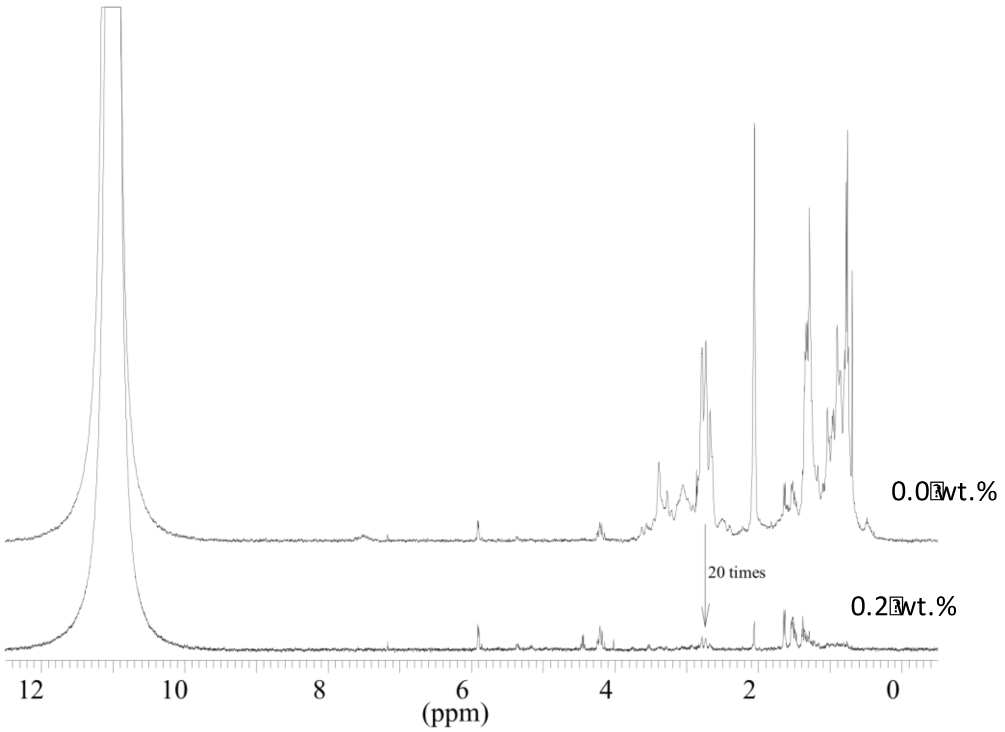


Figure S8 (a) [1]H NMR spectra of H_2SO_4 phase after iC_4 + 1-butene alkylation reaction for pure and DODMAC aided H_2SO_4. ASO amount are 20-40 times less for DODMAC; (b) Cleaned H_2SO_4 phase after alkylation reaction: with DODMAC - left, pure H_2SO_4 - right.

GC analysis

Modified GC method ASTM D5134-98 with variety of heavy products recognition is used to analyze the alkylate mixture. Accurate matching of peaks for numerous C8-9 isomers has been performed using MS-GS experiments. Each GC report includes comprehensive data (lumps) to calculate RON/MON. The mass percent of each component (including heavy ones) are calculated according to the following equation:

mass % component i=((A_i×B_i)/(∑(A_i×B_i))×100,

where: Ai = area of peak for component i and Bi = relative mass response factor for component i. Response factor 1.00 is used for all components except benzene (0.90) and toluene (0.95).

Sample GC analysis data. Isobutane + 1-butene, surfactant DODMAC 0.03% w., T=2˚C, 750 rpm.

Table S3 An example of alkylate phase composition by components. Isobutane + 1-butene, surfactant DODMAC 0.03% w., T=2˚C, 750 rpm.

№	Time, min	Height, mV	Area, mV·min	Concentration, % wt	Component	Group
1	5.372	6445.480	177.810	15.728	Iso-butane	isoButane
2	5.455	11.970	0.620	0.055	Butene-1	nButenes
3	5.606	23.470	0.860	0.076	n-butane	nButane
4	5.680	0.850	0.041	0.004	2,2-Dimethylpropane	2,2-Dimethylpropane
5	6.375	275.840	8.710	0.770	Iso-pentane	isoPentane
6	6.763	0.110	0.010	0.001	Pentane	nPentane
7	7.620	0.150	0.006	0.001	2,2-Dimethylbutane	2,2-Dimethylbutane
8	8.300	373.450	14.630	1.294	2,3-Dimethylbutane	2,3-Dimethylbutane
9	8.387	71.610	3.080	0.273	2-Methylpentane	C6-Monomethyls
10	8.859	34.540	1.500	0.133	3-Methylpentane	C6-Monomethyls
11	9.530	0.280	0.016	0.001	n-hexane	nHexane
12	10.718	249.220	11.870	1.050	2,4-Dimethylpentane	C7-Dimethyls
13	11.080	18.860	0.990	0.088	2,2,3-Trimethylbutane	2,2,3-Trimethylbutane
14	12.186	0.032	0.002	0.000	3,3-Dimethylpentane	C7-Dimethyls
15	12.650	7.760	0.460	0.041	2-Methylhexane	C7-Monomethyls
16	12.812	120.710	6.740	0.596	2,3-Dimethylpentane	C7-Dimethyls
17	13.179	5.580	0.350	0.031	3-Methylhexane	C7-Monomethyls
18	13.837	0.090	0.004	0.000	3-Ethylpentane	C7+
19	14.189	2945.010	309.730	27.396	2,2,4-Trimethylpentane(Iso-octane)	C8-Trimethyls
20	16.960	311.990	21.340	1.888	2,5-Dimethylhexane	C8-Dimethyls
21	17.155	260.980	18.970	1.678	2,4-Dimethylhexane	C8-Dimethyls
22	17.235	421.460	26.390	2.334	2,2,3-Trimethylpentane	C8-Trimethyls
23	18.582	1740.330	196.320	17.365	2,3,4-Trimethylpentane	C8-Trimethyls
24	19.035	2057.580	241.900	21.396	2,3,3-Trimethylpentane	C8-Trimethyls
25	19.272	354.680	22.950	2.030	2,3-Dimethylhexane	C8-Dimethyls
26	19.410	13.790	1.080	0.096	2-Methyl-3-ethylpentane	C8+
27	19.656	5.290	0.390	0.035	2-Methylheptane	C8-Monomethyls
28	19.792	2.310	0.170	0.015	4-Methylheptane	C8-Monomethyls
29	20.009	47.850	4.140	0.366	3,4-Dimethylhexane(L+D)	C8-Dimethyls
30	20.293	6.190	0.430	0.038	3-Methylheptane	C8-Monomethyls
31	20.375	0.560	0.032	0.003	3-Ethylhexane	
32	21.240	54.250	3.900	0.345	2,2,5-Trimethylhexane	C9-Trimethyls
33	22.006	0.490	0.038	0.003	2,2,4-Trimethylhexane	C9-Trimethyls
34	23.266	0.110	0.012	0.001	n-octane	
35	23.608	0.960	0.080	0.007	2,4,4-Trimethylhexane	C9-Trimethyls
36	24.423	8.600	0.750	0.066	2,3,5-Trimethylhexane	C9-Trimethyls
37	25.170	0.350	0.038	0.003	2,4-Dimethylheptane	C9-Dimethyls
38	25.293	0.040	0.001	0.000	2,2,3,4-tetramethylpentane	C9+
39	25.876	0.490	0.041	0.004	2,6-Dimethylheptane	C9-Dimethyls
40	26.240	0.070	0.004	0.000	2-Methyloctane	C9-Monomethyls
41	26.666	1.280	0.130	0.011	2,5-Dimethylheptane	C9-Dimethyls
42	26.794	0.050	0.003	0.000	3,5-Dimethylheptane(D)	C9-Dimethyls
43	26.933	0.090	0.007	0.001	2,3,3-Trimethylhexane	C9-Trimethyls
44	27.067	0.170	0.009	0.001	3,5-Dimethylheptane(L)	C9-Dimethyls

№	Time, min	Height, mV	Area, mV·min	Concentration, % wt	Component	Group
45	28.242	0.490	0.060	0.005	2,3,4-Trimethylhexane	C9-Trimethyls
46	28.473	0.270	0.026	0.002	Methyloctane_1	C9-Monomethyls
47	28.575	0.120	0.007	0.001	Dimethylheptane_1	C9-Dimethyls
48	29.321	0.420	0.040	0.004	2,3-Dimethylheptane	C9-Dimethyls
49	29.620	0.100	0.006	0.001	3,4-Dimethylheptane (D)	C9-Dimethyls
50	29.687	0.110	0.007	0.001	3,4-Dimethylheptane (L)	C9-Dimethyls
51	30.452	0.120	0.010	0.001	4-Methyloctane	C9-Monomethyls
52	31.560	0.032	0.001	0.000	3-Methyloctane	C9-Monomethyls
53	32.168	4.340	0.540	0.048	Trimethylheptane	C10-Trimethyls
54	32.606	6.360	0.680	0.060	2,2-Dimethyloctane	C10-Dimethyls
55	32.730	3.130	0.320	0.028	Trimethylheptane*	C10-Trimethyls
56	33.527	8.560	0.890	0.079	2,2,4-Trimethylheptane	C10-Trimethyls
57	35.114	3.370	0.330	0.029	2,5,5-Trimethylheptane	C10-Trimethyls
58	35.718	0.140	0.014	0.001	3,3-Dimethyloctane	C10-Dimethyls
59	35.912	0.070	0.007	0.001	4,4-Dimethyloctane	C10-Dimethyls
60	36.560	0.240	0.018	0.002	3,4-Dimethyloctane	C10-Dimethyls
61	36.628	0.310	0.034	0.003	3,4,5-Trimethylheptane	C10-Trimethyls
62	37.034	2.920	0.290	0.026	2,3,6-Trimethylheptane	C10-Trimethyls
63	37.249	0.840	0.090	0.008	2,3,5-Trimethylheptane	C10-Trimethyls
64	37.813	0.160	0.012	0.001	Dimethyloctane_1	C10-Dimethyls
65	37.910	0.320	0.025	0.002	2,5-Dimethyloctane	C10-Dimethyls
66	38.100	0.110	0.011	0.001	Dimethyloctane_2	C10-Dimethyls
67	38.323	0.150	0.010	0.001	Dimethyloctane_3	C10-Dimethyls
68	38.483	3.240	0.270	0.024	2,7-Dimethyloctane	C10-Dimethyls
69	38.780	0.240	0.018	0.002	2,6-Dimethyloctane	C10-Dimethyls
70	39.293	0.220	0.024	0.002	3,6-Dimethyloctane	C10-Dimethyls
71	40.083	0.150	0.015	0.001	Dimethyloctane_4	C10-Dimethyls
72	40.335	0.140	0.020	0.002	Dimethyloctane_5	C10-Dimethyls
73	40.562	0.420	0.041	0.004	2-Methyl-3-ethylheptane	C10+
74	41.206	59.210	3.660	0.324	2,2,6-Trimethyloctane	C11-Trimethyls
75	41.628	0.210	0.013	0.001		
76	41.740	0.080	0.005	0.000		
77	41.881	0.130	0.008	0.001		
78	42.016	0.780	0.042	0.004	2,2,6,6-Tetramethylheptane	C11+
79	42.112	12.940	0.780	0.069	2,2,3,5-Tetramethylheptane	C11+
80	42.232	1.340	0.090	0.008	Tetramethylheptane_1	C11+
81	42.345	0.590	0.043	0.004	2,2,3-Trimethyloctane	C11-Trimethyls
82	42.530	1.990	0.120	0.011	Trimethyloctane_1	
83	42.594	1.390	0.090	0.008	Trimethyloctane_2	
84	42.781	0.770	0.050	0.004	Trimethyloctane_3	
85	43.158	0.390	0.019	0.002		
86	43.238	10.650	0.670	0.059	2,3,3-Trimethyloctane	C11-Trimethyls
87	43.373	1.060	0.040	0.004	Trimethyloctane_4	
88	43.431	5.450	0.380	0.034	Trimethyloctane_5	
89	43.517	0.560	0.026	0.002	Trimethyloctane_6	
90	43.730	0.680	0.044	0.004	Trimethyloctane_7	
91	43.890	0.080	0.003	0.000		

№	Time, min	Height, mV	Area, mV·min	Concentration, % wt	Component	Group
92	43.994	0.100	0.005	0.000	Unknown_S	
93	44.106	0.090	0.006	0.001	Tetramethyloctane_1	C12+
94	44.265	0.060	0.003	0.000	2,5-Dimethyldecane	C12-Dimethyls
95	44.388	0.350	0.021	0.002	2,5,6-Trimethyloctane	C11-Trimethyls
96	44.488	19.090	1.010	0.089	2,3,7-Trimethyloctane	C11-Trimethyls
97	44.669	0.670	0.040	0.004	2,3,6-Trimethyloctane	C11-Trimethyls
98	44.703	0.400	0.019	0.002	Trimethyloctane_8	
99	44.827	0.060	0.002	0.000	Trimethyloctane_9	
100	45.008	38.420	1.990	0.176	2,2,4,6,6-Pentamethylheptane	C12+
101	45.332	0.780	0.030	0.003		
102	45.393	27.400	1.410	0.125	Pentamethylheptane_1	C12+
103	45.654	201.340	9.680	0.856	2,3,6,7-Tetramethyloctane	C12+
104	45.776	13.320	0.890	0.079	2,6,8-Trimethyldecane	
105	46.044	2.170	0.180	0.016	5,6-Dimethyldecane	C12-Dimethyls
106	46.291	4.570	0.320	0.028	Tetramethyloctane_2	C12+
107	46.452	9.640	0.720	0.064	5-Ethyl-2,2,3-Trimethylheptane	C12+
108	46.547	191.120	9.550	0.844	Tetramethyloctane_3	C12+
109	46.632	36.430	1.840	0.163	Tetramethyloctane_4	C12+
110	46.836	54.120	2.550	0.226	3,6-Dimethyundecane	
111	46.942	8.570	0.450	0.040	Pentamethylheptane_2	C12+
112	46.989	2.250	0.047	0.004	Pentamethylheptane_3	C12+
113	47.075	7.580	0.540	0.048	2,6-Dimethylundecane	
114	47.209	1.380	0.038	0.003	3,7-Dimethylundecane	
115	47.250	1.820	0.130	0.011	Dimethylundecane_1	
116	47.409	47.130	2.590	0.229	3-Methylundecane	C12-Monomethyls
117	47.462	8.920	0.290	0.026	Tetramethyloctane_5	C12+
118	47.631	3.260	0.150	0.014	5,5-Dimethylundecane	
119	47.714	4.430	0.220	0.019	Tetramethyloctane_6	C12+
120	47.810	15.950	1.080	0.096	Tetramethyloctane_7	C12+
121	47.929	10.830	0.650	0.057	4-Methylundecane	C12-Monomethyls
122	48.062	2.180	0.120	0.011		
123	48.130	6.550	0.330	0.029	Methylundecane_1	C12-Monomethyls
124	48.195	11.390	0.600	0.053	2,3,4-Trimethyldecane	
125	48.243	8.940	0.480	0.042		
126	48.400	0.530	0.020	0.002		
127	48.455	3.240	0.150	0.013	Trimethyldecane_1	
128	48.504	3.460	0.180	0.016	Trimethyldecane_2	
129	48.691	2.800	0.290	0.026	Trimethyldecane_3	
130	48.764	3.590	0.160	0.014	Trimethyldecane_4	
131	48.805	4.490	0.280	0.025	Trimethyldecane_5	
132	48.975	3.630	0.180	0.016	2,2,7-Trimethyldecane	
133	49.000	2.720	0.100	0.009	Trimethyldecane_6	
134	49.140	1.130	0.060	0.005	2,2,6-Trimethyldecane	
135	49.240	0.080	0.003	0.000	Trimethyldecane_7	
136	49.362	0.690	0.039	0.003	Trimethyldecane_8	
137	49.477	2.060	0.130	0.011	Trimethyldecane_9	
138	49.548	1.030	0.060	0.005	4-Methyldodecane	
139	49.667	0.100	0.006	0.000	Trimethyldecane_10	

№	Time, min	Height, mV	Area, mV·min	Concentration, % wt	Component	Group
140	49.759	0.110	0.008	0.001	Trimethyldecane_11	
141	49.957	1.690	0.080	0.007	Trimethyldecane_12	
142	50.005	7.170	0.400	0.035	Trimethyldecane_13	
143	50.185	0.220	0.011	0.001	Trimethyldecane_14	
144	50.257	0.280	0.012	0.001	Trimethyldecane_15	
145	50.328	0.500	0.031	0.003	Trimethyldecane_16	
146	50.473	0.050	0.002	0.000	2,6,6-Trimethyldecane	
147	50.562	1.910	0.100	0.008	2,6,10-Trimethyldodecane	
148	50.623	1.470	0.070	0.006	2,2,5-Trimethyldodecane	
149	50.745	0.610	0.037	0.003		
150	50.825	0.210	0.014	0.001		
151	50.994	0.230	0.014	0.001		
152	51.075	0.140	0.009	0.001		
153	51.398	0.210	0.015	0.001		
154	51.558	0.090	0.005	0.000		
155	51.660	0.310	0.016	0.001		
156	51.830	0.180	0.018	0.002		
157	52.042	0.220	0.010	0.001		
158	52.160	0.270	0.017	0.002		
159	52.580	0.120	0.003	0.000		
160	52.687	0.110	0.006	0.001		
161	53.134	0.250	0.008	0.001		
162	53.240	0.420	0.018	0.002		
163	53.657	0.390	0.015	0.001		
164	53.817	0.380	0.012	0.001		
165	53.914	0.350	0.015	0.001		
166	53.979	0.330	0.011	0.001		
167	54.531	0.880	0.042	0.004		
168	54.765	0.950	0.046	0.004		
169	54.933	3.870	0.200	0.018		
170	55.148	0.690	0.050	0.005		
171	55.223	1.190	0.090	0.008		
172	55.396	1.280	0.100	0.009		
173	55.460	0.820	0.050	0.005		
174	55.638	0.460	0.023	0.002		
175	55.779	1.400	0.090	0.008		
176	55.858	0.870	0.070	0.006		
177	56.065	0.600	0.027	0.002		
178	56.120	0.640	0.041	0.004		
179	56.232	0.920	0.050	0.005		
180	56.616	0.670	0.060	0.005		
181	56.890	0.920	0.100	0.009		
182	56.965	1.110	0.110	0.009		
183	57.220	0.700	0.080	0.007		
184	57.435	0.730	0.060	0.005		
185	57.576	0.400	0.026	0.002		
186	57.736	0.340	0.017	0.001		
187	57.870	0.250	0.011	0.001		

Table S4 Alkylate phase composition by lumps. Isobutane + 1-butene, surfactant DODMAC 0.03% w., T=2˚C, 750 rpm.

Area, mV·min	Concentration, % wt	Group	Area, mV·min	Concentration, % wt	Group
0.860	0.076	nButane	0.000	0.000	C10-Monomethyls
0.010	0.001	nPentane	1.120	0.099	C10-Dimethyls
0.016	0.001	nHexane	2.500	0.221	C10-Trimethyls
177.810	15.728	isoButane	0.000	0.000	C11-Monomethyls
8.710	0.770	isoPentane	0.000	0.000	C11-Dimethyls
0.041	0.004	2,2-Dimethylpropane	5.440	0.482	C11-Trimethyls
4.590	0.406	C6-Monomethyls	3.570	0.316	C12-Monomethyls
0.006	0.001	2,2-Dimethylbutane	0.180	0.016	C12-Dimethyls
14.630	1.294	2,3-Dimethylbutane	0.000	0.000	C12-Trimethyls
0.810	0.071	C7-Monomethyls	0.620	0.055	nButenes
18.610	1.646	C7-Dimethyls	0.000	0.000	nPentenes
0.990	0.088	2,2,3-Trimethylbutane	0.004	0.000	C7+
1.000	0.088	C8-Monomethyls	1.080	0.096	C8+
67.400	5.962	C8-Dimethyls	0.001	0.000	C9+
774.340	68.491	C8-Trimethyls	0.041	0.004	C10+
0.041	0.004	C9-Monomethyls	0.920	0.081	C11+
0.280	0.025	C9-Dimethyls	27.600	2.442	C12+
4.840	0.428	C9-Trimethyls			

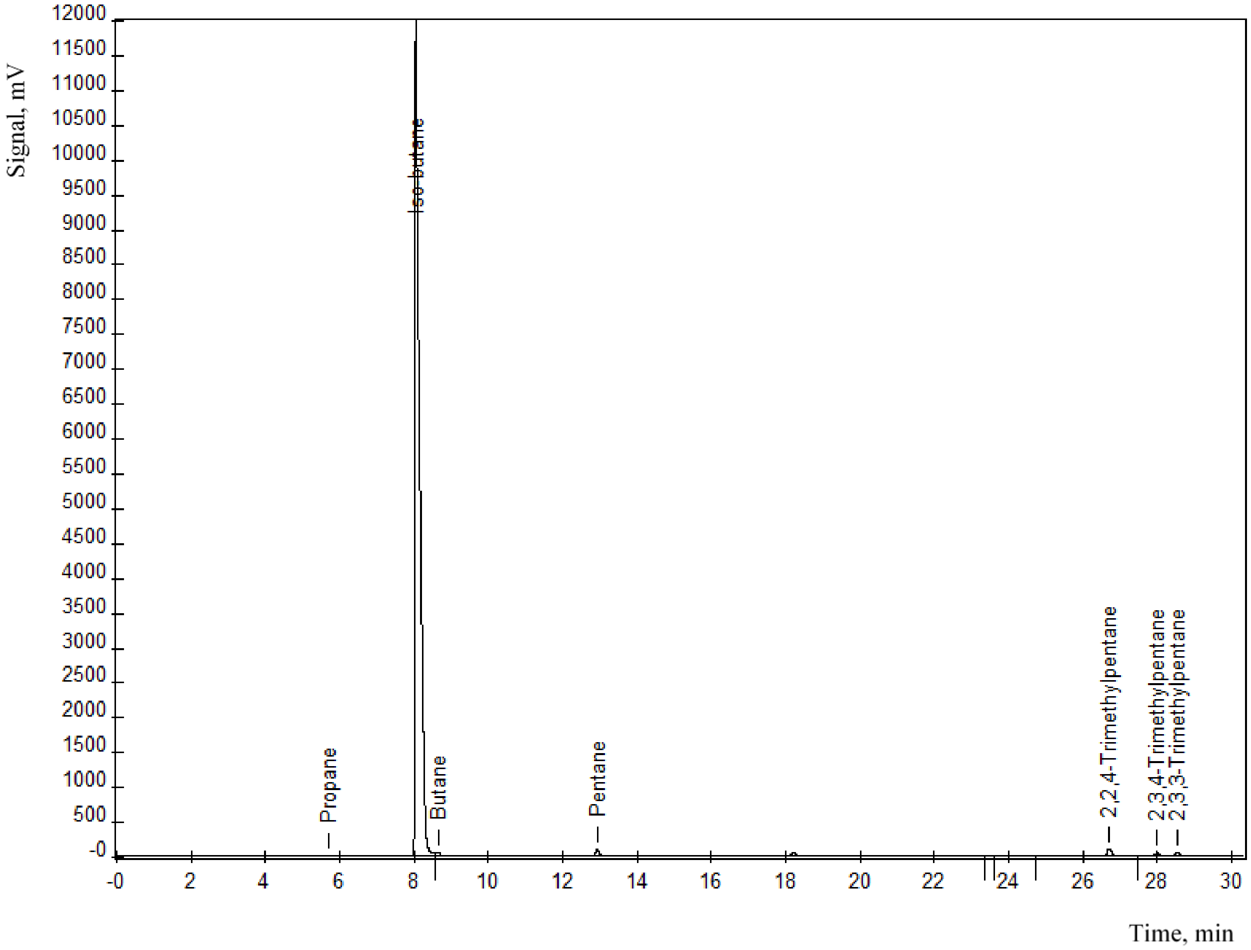


Figure S9 An example of gaseous phase GC analysis. Isobutane + 1-butene, surfactant DODMAC 0.03% w., T=2˚C, 750 rpm.

Table S5 Gaseous phase composition by components. Isobutane + 1-butene, surfactant DODMAC 0.03% w., T=2˚C, 750 rpm.

№	Time, mins	Height, mV	Area, mV·min	Concentration, % wt	Component
1	5.689	6.26	0.38	0.021	Propane
2	8.04	11777.52	1745.44	96.139	Iso-butane
3	8.648	53.75	9.31	0.513	Butane
4	12.929	106.63	13.34	0.735	Pentane
5	18.21	61.22	9.06	0.499	
6	22.429	10.41	1.48	0.081	
7	23.293	1.93	0.41	0.023	
8	23.522	5.41	0.95	0.053	
9	23.629	3.62	0.67	0.037	
10	24.585	2.23	0.7	0.039	
11	24.951	3.59	0.98	0.054	
12	26.722	107.57	16.31	0.898	Iso-octane
13	27.383	3.21	0.52	0.028	
14	27.57	3.43	0.5	0.027	
15	28.002	48.62	7.93	0.437	2,3,4-Trimethylpentane
16	28.527	46.74	7.55	0.416	2,3,3-Trimethylpentane

Sample GC analysis data. Isobutane + 1-butene, no surfactants, synthetic ASO added. T=2˚C, 750 rpm.

Table S6 – Alkylate phase composition by components. Isobutane + 1-butene ASO, no additional surfactant, T=2˚C, 750 rpm.

№	Time, mins	Height, mV	Area, mV·min	Concentration, % wt	Component	Group
1	5.371	2274.770	62.750	5.232	Iso-butane	isoButane
2	5.470	6.610	0.370	0.031	Butene-1	nButenes
3	5.604	10.850	0.450	0.037	n-butane	nButane
4	5.683	0.320	0.012	0.001	2,2-Dimethylpropane	2,2-Dimethylpropane
5	6.384	594.000	18.990	1.583	Iso-pentane	isoPentane
6	6.623	0.690	0.050	0.004	Pentane	nPentane
7	6.792	0.290	0.015	0.001		
8	7.550	0.560	0.023	0.002	2,2-Dimethylbutane	2,2-Dimethylbutane
9	8.331	610.950	23.820	1.986	2,3-Dimethylbutane	2,3-Dimethylbutane
10	8.417	223.360	9.230	0.769	2-Methylpentane	C6-Monomethyls
11	8.889	99.250	4.170	0.348	3-Methylpentane	C6-Monomethyls
12	10.760	403.820	19.250	1.605	2,4-Dimethylpentane	C7-Dimethyls
13	11.111	73.000	3.760	0.313	2,2,3-Trimethylbutane	2,2,3-Trimethylbutane
14	12.087	0.015	0.000	0.000	3,3-Dimethylpentane	C7-Dimethyls
15	12.675	79.590	4.220	0.352	2-Methylhexane	C7-Monomethyls
16	12.848	201.610	11.080	0.924	2,3-Dimethylpentane	C7-Dimethyls
17	13.200	52.710	2.910	0.242	3-Methylhexane	C7-Monomethyls
18	13.854	1.440	0.090	0.007	3-Ethylpentane	C7+
19	14.172	1959.670	162.860	13.578	2,2,4-Trimethylpentane(Iso-octane)	C8-Trimethyls
20	15.152	0.038	0.000	0.000	n-heptane	
21	16.984	467.880	31.730	2.646	2,5-Dimethylhexane	C8-Dimethyls
22	17.166	372.950	26.170	2.182	2,4-Dimethylhexane	C8-Dimethyls
23	17.244	231.210	12.700	1.059	2,2,3-Trimethylpentane	C8-Trimethyls
24	18.512	877.010	70.670	5.892	2,3,4-Trimethylpentane	C8-Trimethyls
25	18.948	1110.150	96.470	8.043	2,3,3-Trimethylpentane	C8-Trimethyls
26	19.250	394.580	26.440	2.204	2,3-Dimethylhexane	C8-Dimethyls
27	19.385	14.570	1.050	0.087	2-Methyl-3-ethylpentane	C8+
28	19.627	26.560	1.730	0.144	2-Methylheptane	C8-Monomethyls
29	19.765	7.750	0.520	0.043	4-Methylheptane	C8-Monomethyls
30	19.994	51.600	4.460	0.372	3,4-Dimethylhexane(L+D)	C8-Dimethyls
31	20.269	20.820	1.410	0.117	3-Methylheptane	C8-Monomethyls
32	20.388	1.550	0.110	0.009	3-Ethylhexane	
33	20.707	4.380	0.330	0.027		
34	20.876	2.680	0.220	0.018		
35	21.346	1166.540	127.020	10.590	2,2,5-Trimethylhexane	C9-Trimethyls
36	21.988	11.400	0.850	0.071	2,2,4-Trimethylhexane	C9-Trimethyls
37	22.523	0.940	0.070	0.006		
38	23.177	0.570	0.047	0.004	n-octane	
39	23.562	18.000	1.480	0.124	2,4,4-Trimethylhexane	C9-Trimethyls
40	24.400	167.040	14.340	1.196	2,3,5-Trimethylhexane	C9-Trimethyls
41	25.105	30.400	2.600	0.217	2,4-Dimethylheptane	C9-Dimethyls
42	25.270	1.260	0.120	0.010	2,2,3,4-tetramethylpentane	C9+
43	25.811	54.960	4.860	0.405	2,6-Dimethylheptane	C9-Dimethyls
44	26.095	3.750	0.370	0.031	2-Methyloctane	C9-Monomethyls
45	26.612	96.000	9.440	0.787	2,5-Dimethylheptane	C9-Dimethyls
46	26.795	16.560	1.660	0.139	3,5-Dimethylheptane(D)	C9-Dimethyls
47	27.005	5.680	0.510	0.043	2,3,3-Trimethylhexane	C9-Trimethyls

№	Time, mins	Height, mV	Area, mV·min	Concentration, % wt	Component	Group
48	27.122	7.300	0.730	0.061	3,5-Dimethylheptane(L)	C9-Dimethyls
49	28.160	7.590	0.860	0.072	2,3,4-Trimethylhexane	C9-Trimethyls
50	28.381	3.610	0.360	0.030	Methyloctane_1	C9-Monomethyls
51	28.661	16.600	1.710	0.143	Dimethylheptane_1	C9-Dimethyls
52	29.224	22.130	2.290	0.191	2,3-Dimethylheptane	C9-Dimethyls
53	29.539	3.770	0.340	0.028	3,4-Dimethylheptane (D)	C9-Dimethyls
54	29.626	4.130	0.420	0.035	3,4-Dimethylheptane (L)	C9-Dimethyls
55	30.208	1.900	0.190	0.016		
56	30.333	2.860	0.330	0.027	4-Methyloctane	C9-Monomethyls
57	31.147	0.340	0.021	0.002		
58	31.324	1.950	0.220	0.018	3-Methyloctane	C9-Monomethyls
59	32.084	42.170	6.930	0.578	Trimethylheptane	C10-Trimethyls
60	32.581	218.500	24.900	2.076	2,2-Dimethyloctane	C10-Dimethyls
61	32.671	40.870	2.880	0.240	Trimethylheptane*	C10-Trimethyls
62	33.490	205.710	21.270	1.773	2,2,4-Trimethylheptane	C10-Trimethyls
63	33.926	0.960	0.080	0.006		
64	35.050	138.040	12.740	1.062	2,5,5-Trimethylheptane	C10-Trimethyls
65	35.619	0.970	0.080	0.006	3,3-Dimethyloctane	C10-Dimethyls
66	35.825	10.050	0.910	0.076	4,4-Dimethyloctane	C10-Dimethyls
67	36.469	7.920	0.700	0.058	3,4-Dimethyloctane	C10-Dimethyls
68	36.552	7.660	0.580	0.048	3,4,5-Trimethylheptane	C10-Trimethyls
69	36.953	79.530	7.420	0.618	2,3,6-Trimethylheptane	C10-Trimethyls
70	37.157	17.670	1.620	0.135	2,3,5-Trimethylheptane	C10-Trimethyls
71	37.716	9.830	0.720	0.060	Dimethyloctane_1	C10-Dimethyls
72	37.806	17.520	1.410	0.117	2,5-Dimethyloctane	C10-Dimethyls
73	37.979	7.170	0.740	0.062	Dimethyloctane_2	C10-Dimethyls
74	38.209	5.660	0.430	0.036	Dimethyloctane_3	C10-Dimethyls
75	38.388	21.090	2.150	0.179	2,7-Dimethyloctane	C10-Dimethyls
76	38.670	19.820	1.610	0.134	2,6-Dimethyloctane	C10-Dimethyls
77	38.850	1.020	0.070	0.006		
78	39.005	0.480	0.032	0.003		
79	39.178	6.840	0.820	0.069	3,6-Dimethyloctane	C10-Dimethyls
80	39.400	1.080	0.090	0.007		
81	39.925	1.820	0.120	0.010		
82	39.985	2.340	0.180	0.015	Dimethyloctane_4	C10-Dimethyls
83	40.238	2.340	0.220	0.018	Dimethyloctane_5	C10-Dimethyls
84	40.461	7.430	0.650	0.054	2-Methyl-3-ethylheptane	C10+
85	40.825	1.030	0.090	0.007		
86	40.914	1.000	0.070	0.006		
87	41.168	425.400	28.710	2.393	2,2,6-Trimethyloctane	C11-Trimethyls
88	41.558	1.970	0.120	0.010		
89	41.648	0.800	0.046	0.004		
90	41.798	2.020	0.140	0.012		
91	41.944	77.920	4.420	0.369	2,2,6,6-Tetramethylheptane	C11+
92	42.041	85.220	5.240	0.437	2,2,3,5-Tetramethylheptane	C11+
93	42.160	73.140	4.510	0.376	Tetramethylheptane_1	C11+
94	42.270	38.070	2.350	0.196	2,2,3-Trimethyloctane	C11-Trimethyls
95	42.460	137.580	7.830	0.653	Trimethyloctane_1	
96	42.530	100.580	5.600	0.467	Trimethyloctane_2	

№	Time, mins	Height, mV	Area, mV·min	Concentration, % wt	Component	Group
97	42.714	6.410	0.370	0.031	Trimethyloctane_3	
98	42.896	1.370	0.090	0.007		
99	43.080	2.990	0.150	0.013		
100	43.166	61.230	3.570	0.297	2,3,3-Trimethyloctane	C11-Trimethyls
101	43.275	57.630	3.310	0.276	Trimethyloctane_4	
102	43.356	31.380	1.930	0.161	Trimethyloctane_5	
103	43.448	20.900	1.380	0.115	Trimethyloctane_6	
104	43.650	55.090	3.120	0.260	Trimethyloctane_7	
105	43.819	1.780	0.100	0.009		
106	43.920	5.350	0.280	0.024	Unknown_S	
107	44.036	5.810	0.290	0.024	Tetramethyloctane_1	C12+
108	44.190	9.190	0.540	0.045	2,5-Dimethyldecane	C12-Dimethyls
109	44.302	12.800	0.690	0.057	2,5,6-Trimethyloctane	C11-Trimethyls
110	44.420	53.300	2.680	0.224	2,3,7-Trimethyloctane	C11-Trimethyls
111	44.590	22.320	1.090	0.091	2,3,6-Trimethyloctane	C11-Trimethyls
112	44.645	16.030	0.770	0.064	Trimethyloctane_8	
113	44.745	3.130	0.130	0.011	Trimethyloctane_9	
114	44.842	3.090	0.150	0.013		
115	44.956	416.640	21.970	1.832	2,2,4,6,6-Pentamethylheptane	C12+
116	45.183	3.230	0.140	0.012		
117	45.239	4.570	0.280	0.023		
118	45.327	146.020	7.320	0.610	Pentamethylheptane_1	C12+
119	45.587	167.260	8.340	0.695	2,3,6,7-Tetramethyloctane	C12+
120	45.710	55.320	3.790	0.316	2,6,8-Trimethyldecane	
121	45.972	19.390	1.780	0.148	5,6-Dimethyldecane	C12-Dimethyls
122	46.215	39.240	1.940	0.162	Tetramethyloctane_2	C12+
123	46.387	66.380	5.260	0.439	5-Ethyl-2,2,3-Trimethylheptane	C12+
124	46.479	113.390	5.740	0.479	Tetramethyloctane_3	C12+
125	46.565	83.420	4.200	0.350	Tetramethyloctane_4	C12+
126	46.780	333.570	16.280	1.358	3,6-Dimethyundecane	
127	46.875	32.510	1.390	0.116	Pentamethylheptane_2	C12+
128	46.926	37.490	1.890	0.158	Pentamethylheptane_3	C12+
129	46.996	27.700	1.790	0.149	2,6-Dimethylundecane	
130	47.145	30.530	1.180	0.099	3,7-Dimethylundecane	
131	47.181	34.720	2.430	0.203	Dimethylundecane_1	
132	47.348	317.840	17.940	1.495	3-Methylundecane	C12-Monomethyls
133	47.398	67.470	2.520	0.210	Tetramethyloctane_5	C12+
134	47.562	13.080	0.570	0.048	5,5-Dimethylundecane	
135	47.642	58.170	2.870	0.239	Tetramethyloctane_6	C12+
136	47.737	36.550	2.730	0.228	Tetramethyloctane_7	C12+
137	47.856	69.500	3.560	0.296	4-Methylundecane	C12-Monomethyls
138	47.985	1.480	0.049	0.004		
139	48.058	33.090	1.390	0.116	Methylundecane_1	C12-Monomethyls
140	48.122	48.810	2.540	0.212	2,3,4-Trimethyldecane	
141	48.170	43.430	2.060	0.172		
142	48.336	12.320	0.610	0.051	Trimethyldecane_1	
143	48.398	25.090	1.610	0.134	Trimethyldecane_2	
144	48.539	19.800	1.100	0.091	Trimethyldecane_3	
145	48.618	9.050	0.250	0.021		

№	Time, mins	Height, mV	Area, mV·min	Concentration, % wt	Component	Group
146	48.667	41.450	2.260	0.189	Trimethyldecane_4	
147	48.734	17.160	0.910	0.075	Trimethyldecane_5	
148	48.923	59.330	3.100	0.259	2,2,7-Trimethyldecane	
149	48.970	43.000	1.780	0.149	Trimethyldecane_6	
150	49.068	218.290	11.040	0.920	2,2,6-Trimethyldecane	
151	49.167	20.260	0.830	0.069	Trimethyldecane_7	
152	49.252	34.280	1.510	0.126	Trimethyldecane_8	
153	49.311	8.260	0.300	0.025		
154	49.417	48.510	2.640	0.220	Trimethyldecane_9	
155	49.511	10.120	0.450	0.037	4-Methyldodecane	
156	49.581	24.490	1.110	0.093	Trimethyldecane_10	
157	49.697	13.750	0.940	0.079	Trimethyldecane_11	
158	49.791	7.330	0.320	0.027	Trimethyldecane_12	
159	49.955	13.870	0.820	0.069	Trimethyldecane_13	
160	50.111	34.170	1.810	0.151	Trimethyldecane_14	
161	50.176	34.760	1.680	0.140	Trimethyldecane_15	
162	50.252	32.090	1.600	0.134	Trimethyldecane_16	
163	50.292	8.640	0.280	0.024	2,6,6-Trimethyldecane	
164	50.500	383.420	19.560	1.631	2,6,10-Trimethyldodecane	
165	50.563	325.280	15.090	1.258	2,2,5-Trimethyldodecane	
166	50.680	33.670	1.750	0.146		
167	50.746	14.330	0.890	0.074		
168	50.919	29.200	1.710	0.143		
169	50.995	16.120	0.890	0.075		
170	51.142	19.030	1.120	0.094		
171	51.320	31.540	1.680	0.140		
172	51.483	16.300	1.200	0.100		
173	51.584	36.980	1.800	0.150		
174	51.740	6.010	0.330	0.028		
175	51.805	13.000	0.760	0.063		
176	51.924	8.330	0.250	0.021		
177	51.972	56.240	2.890	0.241		
178	52.085	33.670	2.350	0.196		
179	52.245	3.210	0.140	0.012		
180	52.319	4.520	0.170	0.014		
181	52.444	9.440	0.450	0.038		
182	52.518	4.950	0.190	0.016		
183	52.618	7.710	0.320	0.027		
184	52.720	3.400	0.120	0.010		
185	52.846	6.910	0.440	0.037		
186	53.000	38.570	1.700	0.142		
187	53.055	42.250	2.130	0.177		
188	53.175	122.310	6.460	0.538		
189	53.296	5.020	0.250	0.021		
190	53.496	33.750	1.650	0.138		
191	53.570	50.320	2.510	0.210		
192	53.668	10.880	0.570	0.047		
193	53.764	3.770	0.160	0.014		
194	53.808	5.440	0.220	0.018		

№	Time, mins	Height, mV	Area, mV·min	Concentration, % wt	Component	Group
195	53.909	12.770	0.540	0.045		
196	53.960	15.810	0.880	0.074		
197	54.008	13.320	0.580	0.048		
198	54.152	1.960	0.080	0.007		
199	54.260	7.850	0.510	0.043		
200	54.411	10.690	0.510	0.042		
201	54.461	14.890	0.750	0.062		
202	54.615	3.350	0.190	0.016		
203	54.694	14.720	0.830	0.070		
204	54.768	5.970	0.290	0.024		
205	54.862	64.020	3.440	0.287		
206	55.004	10.190	0.710	0.059		
207	55.094	13.370	0.570	0.047		
208	55.140	28.050	2.080	0.174		
209	55.295	23.810	1.260	0.105		
210	55.321	25.620	1.240	0.104		
211	55.386	11.640	0.440	0.036		
212	55.435	16.010	0.830	0.069		
213	55.532	4.810	0.180	0.015		
214	55.575	7.620	0.380	0.031		
215	55.620	6.130	0.250	0.020		
216	55.705	16.800	1.060	0.088		
217	55.785	12.570	0.710	0.059		
218	55.857	3.020	0.110	0.009		
219	55.961	16.950	1.000	0.083		
220	56.081	4.860	0.260	0.022		
221	56.160	10.050	0.660	0.055		
222	56.435	10.000	1.030	0.086		
223	56.623	5.220	0.240	0.020		
224	56.707	4.860	0.250	0.020		
225	56.830	8.900	0.710	0.059		
226	56.934	7.230	0.450	0.037		
227	57.010	9.540	0.520	0.044		
228	57.119	6.950	0.400	0.033		
229	57.183	3.150	0.110	0.010		
230	57.280	6.860	0.560	0.047		
231	57.364	7.070	0.730	0.061		
232	57.512	5.060	0.440	0.037		
233	57.645	1.680	0.070	0.006		
234	57.705	1.820	0.080	0.007		
235	57.841	3.790	0.190	0.016		
236	57.878	5.490	0.280	0.023		
237	57.930	6.040	0.290	0.024		
238	58.001	5.610	0.300	0.025		
239	58.079	4.480	0.370	0.031		
240	58.230	0.620	0.019	0.002		
241	58.288	1.450	0.070	0.006		
242	58.534	2.960	0.170	0.015		
243	58.665	15.850	0.880	0.073		

Table S7 Alkylate phase composition by lumps. Isobutane + 1-butene ASO, no additional surfactant, T=2˚C, 750 rpm.

Area, mV·min	Concentration, % wt	Group	Area, mV·min	Concentration, % wt	Group
0.450	0.037	nButane	0.000	0.000	C10-Monomethyls
0.050	0.004	nPentane	34.860	2.907	C10-Dimethyls
0.000	0.000	nHexane	53.440	4.455	C10-Trimethyls
62.750	5.232	isoButane	0.000	0.000	C11-Monomethyls
18.990	1.583	isoPentane	0.000	0.000	C11-Dimethyls
0.012	0.001	2,2-Dimethylpropane	39.090	3.259	C11-Trimethyls
13.400	1.117	C6-Monomethyls	22.880	1.907	C12-Monomethyls
0.023	0.002	2,2-Dimethylbutane	2.310	0.193	C12-Dimethyls
23.820	1.986	2,3-Dimethylbutane	0.000	0.000	C12-Trimethyls
7.130	0.595	C7-Monomethyls	0.370	0.031	nButenes
30.330	2.529	C7-Dimethyls	0.000	0.000	nPentenes
3.760	0.313	2,2,3-Trimethylbutane	0.090	0.007	C7+
3.660	0.305	C8-Monomethyls	1.050	0.087	C8+
88.810	7.405	C8-Dimethyls	0.120	0.010	C9+
342.700	28.573	C8-Trimethyls	0.650	0.054	C10+
1.270	0.106	C9-Monomethyls	14.170	1.182	C11+
24.050	2.005	C9-Dimethyls	66.460	5.541	C12+
145.070	12.095	C9-Trimethyls			

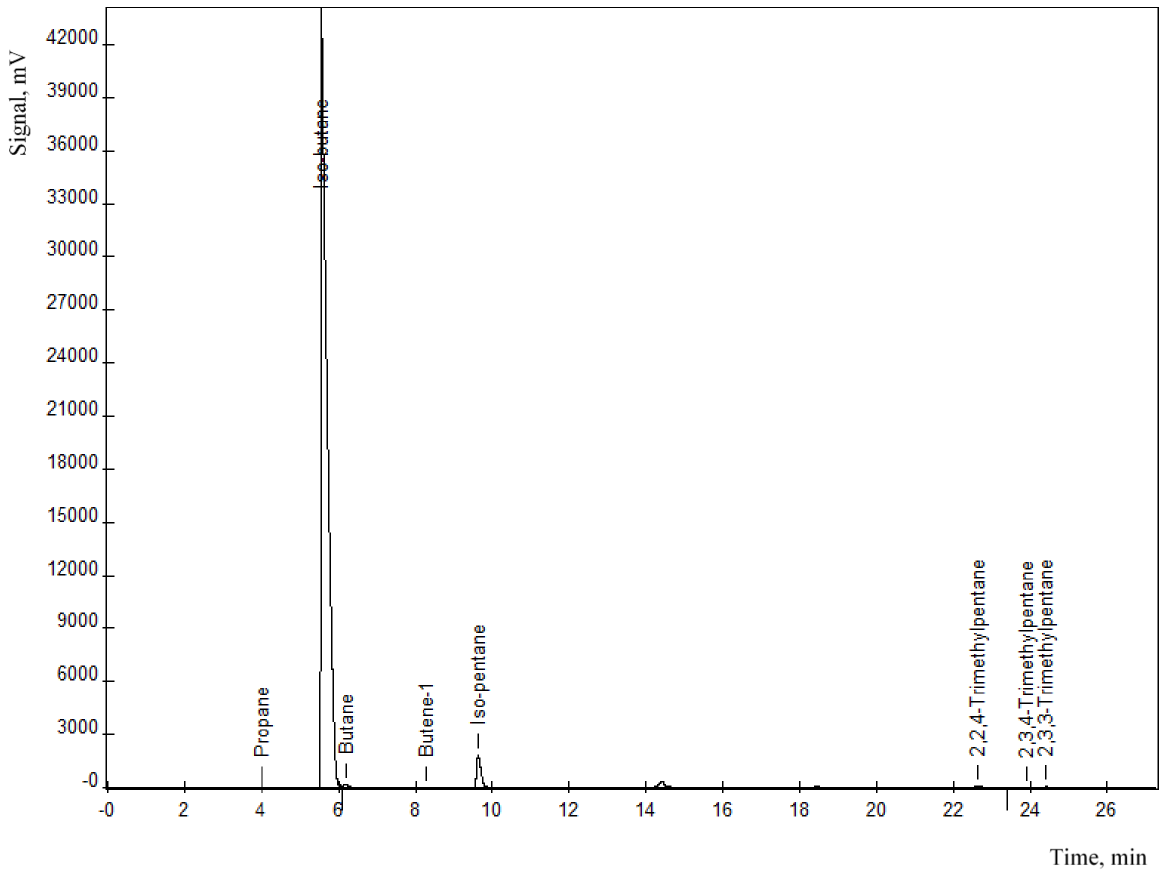


Figure S10 An example of gaseous phase GC analysis. Isobutane + 1-butene ASO, no additional surfactant, T=2˚C, 750 rpm.

Table S8 Alkylate phase composition by components. Isobutane + 1-butene ASO, no additional surfactant, T=2˚C, 750 rpm.

№	Time, mins	Height, mV	Area, mV·min	Concentration, % wt	Component
1	4.005	2.910	0.140	0.002	Propane
2	5.557	43923.020	7854.130	95.520	Iso-butane
3	6.190	184.150	30.030	0.365	Butane
4	8.273	8.780	0.790	0.010	Butene-1
5	9.640	1835.550	233.800	2.843	Iso-pentane
6	14.404	351.870	67.820	0.825	
7	18.448	37.430	5.710	0.069	
8	19.477	13.090	3.020	0.037	
9	22.639	98.110	15.810	0.192	Iso-octane
10	23.325	4.540	0.630	0.008	
11	23.525	5.470	0.820	0.010	
12	23.921	25.720	4.940	0.060	2,3,4-Trimethylpentane
13	24.418	29.860	4.900	0.060	2,3,3-Trimethylpentane

References

S1 L. F. Albright, L. Houle, A. M. Sumutka and R. E. Eckert, *Ind. Eng. Chem. Process Des. Dev.*, 1972, 11, 446; https://doi.org/10.1021/i260043a020.

S2 F. R. Alves, W. Loh, M. E. D. Zaniquelli, E. M. S. Castanheira, M. E. C. D. Real Oliveira and E. Feitosa, *J. Colloid Interface Sci.*, 2007, 316, 132; https://doi.org/10.1016/j.jcis.2007.08.027.