Efficient Non-catalytic Oxidative and Extractive Desulfurization of Liquid Fuels using Ionic Liquids

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Supplementary Information

Kinetic studies

Table S1: Kinetic parameters of fitted data (DBT)

Temp., °C	$k_{1\,(DBT)}$, g/(mol s)	R^2	$k_{2\,(DBT)} \times 10^{-7}$, $g^2/(mol\ s)^2$	R^2
30.0	71.6	0.9988	1.4	0.9724
37.5	102.5	0.9993	2.0	0.9832
40.0	182.8	0.9976	4.2	0.9872

k_1: second order rate constant. k_2: third order rate constant.

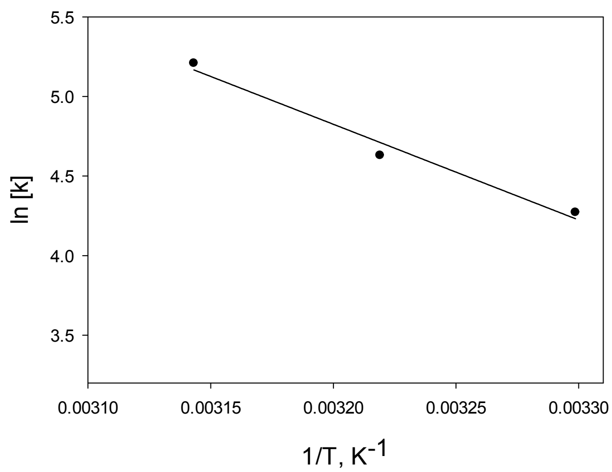

Figure S1: Arrhenius plot for DBT second order kinetic model

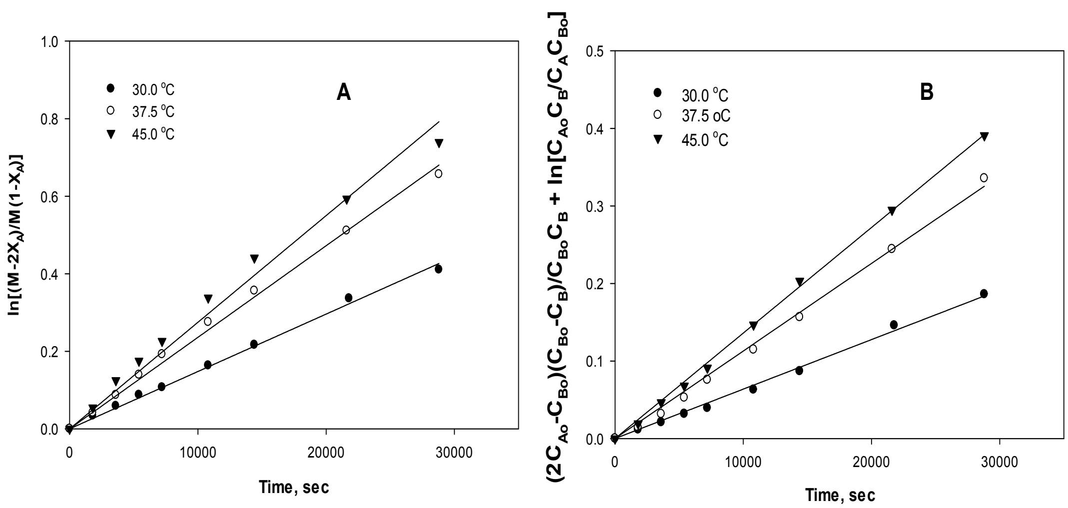

Figure S2: A- The plot of ln [(M-2X_A)/(M(1-X_A)] versus time at different temperature (Bimolecular), M=3. B- The plot of (2C_{Ao}-C_{Bo})(C_{Bo}-C_B)/(C_{Bo} C_B)+ln[C_{Ao} C_B)/C_A C_{Bo}] against time at different temperature (Trimolecular) for BT.

Table S2: Kinetic parameters of fitted data (BT)

Temp., °C	$k_{1\,(BT)}$, g/(mol s)	R^2	$k_{2\,(BT)} \times 10^{-5}$, $g^2/(mol\ s)^2$	R^2
30.0	3.5	0.9960	3.5	0.9948
37.5	5.6	0.9952	6.2	0.9960
40.0	6.5	0.9825	7.7	0.9989

k_1: second order rate constant. k_2: third order rate constant.

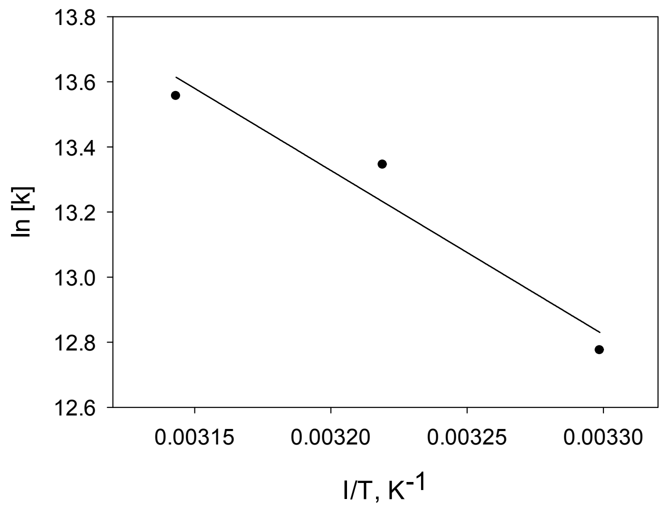

Figure S3: Arrhenius plot for BT second order kinetic model

$$r_{BT} = k_{BT}C_{BT}C_{mCPBA}^{2}, \quad k_{BT} = 6.21 \times 10^{12}e^{-41905/RT} \qquad \textbf{S1}$$

Preliminary extractive and oxidative desulfurization experiment ($[P_{i444,1}]$[Tos])

The comparison between the EDS and EODS as function of reaction time using the $[P_{i444,1}]$[Tos] (Figure S4) shows an improvement upon addition of an oxidation step for both %SR (BT) and %SR (DBT). For BT after 120 min of EODS experiment, SR increased from 57% to 60%. The corresponding increase for DBT was 59% to 76%.

Figure S5 shows the comparison between EDS and EODS as functions of temperature. It can be seen that although the %SR (BT) in EODS increases with reaction temperature, the improvement was not as desired, going from 54% to 68% at 80 ^{o}C and from 53% to 64% at 60 ^{o}C. For DBT, the increase was from 62% to 98% at 80 ^{o}C and 62% to 90% at 60 ^{o}C.

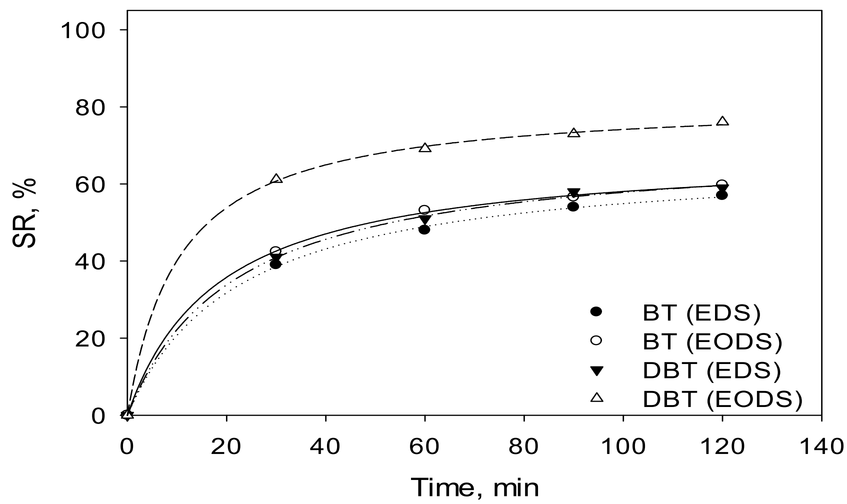

Figure S4: Comparison between EDS and EODS as a function of time using [P$_{i444,1}$][Tos] at 30 ^{o}C, 600 rpm

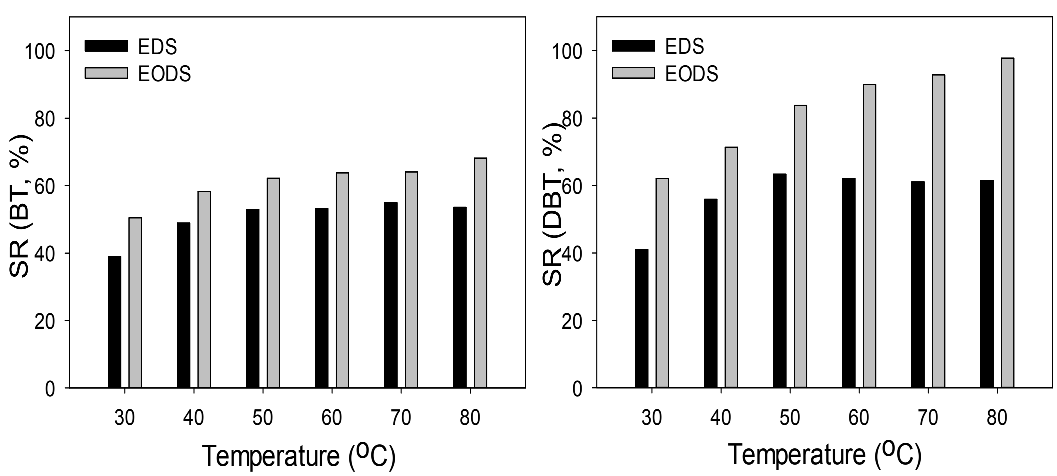

Figure S5: Comparison between EDS and EODS as a function of temperature using [P$_{i444,1}$][Tos] at 30 min, 600 rpm

Optimization of the EODS of simulated fuel using [P$_{i444,1}$][Tos])

Table S3 and Table S4 show the design matrix for the EODS of BT and DBT, respectively, using [P$_{i444,1}$][Tos]. This resulted in 30 experimental runs, responses of which were fitted to a quadratic model. Table S5 shows the ANOVA of the EODS of BT using the [P$_{i444,1}$][Tos] IL. The model was found to be significant with an F value of 45.3 and p-value of < 0.01%. All independent variables possess significant effect on the efficiency of the process. Furthermore, the mass fraction is the most significant term (F value ≈ 180).

Reaction temperature is the next most significant variable (F value ≈ 61) followed by reaction time (F value ≈ 55) and O/S (F value ≈ 7). Other significant terms include time-O/S, temperature-mass fraction and temperature-O/S. No second order term is significant and as result the model was reduced to two factor interaction (2FI) model. The model, adjusted and predicted R^2 were found to be 0.9411, 0.9199 and 0.7881 respectively. The plot of predicted response (SR) against the experimental response is shown in Figure S6.

Table S6 present the ANOVA of the EODS of DBT using $[P_{i444,1}]$[Tos] IL. Similarly the model is significant with F value of ~63 and p-value of <0.01%. All the independent variables are significant model terms with reaction temperature being the most significant with F value of ~310 followed by reaction time with an F value of ~208. All interaction terms are significant with the exception of time-O/S and temperature-O/S. The second order terms of all the independent variables are significant with the exception of mass fraction. The model R^2 was calculated as 0.9793 while the adjusted and predicted R^2 were found to be 0.9619 and 0.9073 respectively.

Table S3: Experimental design matrix for EODS of BT using [$P_{i444,1}$][Tos]

Run	Coded Values				Actual Values				%SR	
	X_1	X_2	X_3	X_4	X_1	X_2	X_3	X_4	Y_{exp}	R*
1	0	0	0	0	47.5	45	0.67	6	53.01	4.88
2	1	-1	-1	-1	80.0	30	0.50	3	63.16	1.70
3	-1	-1	-1	1	15.0	30	0.50	9	46.81	0.11
4	-1	1	1	1	15.0	60	0.83	9	30.38	-10.14
5	1	1	-1	1	80.0	60	0.50	9	78.62	-3.51
6	-1	-1	1	-1	15.0	30	0.83	3	20.91	1.86
7	1	1	1	-1	80.0	60	0.83	3	48.50	3.51
8	-1	1	-1	-1	15.0	60	0.50	3	58.41	1.94
9	1	-1	1	1	80.0	30	0.83	9	29.04	-5.05
10	0	0	0	0	47.5	45	0.67	6	52.83	4.69
11	1	1	-1	-1	80.0	60	0.50	3	62.38	-4.31
12	0	0	0	0	47.5	45	0.67	6	49.19	1.83
13	-1	-1	-1	-1	15.0	30	0.50	3	45.50	-4.19
14	-1	1	-1	1	15.0	60	0.50	9	65.71	3.50
15	1	-1	1	-1	80.0	30	0.83	3	25.81	-3.13
16	1	-1	-1	1	80.0	30	0.50	9	63.85	-1.22
17	-1	1	1	-1	15.0	60	0.83	3	29.53	-3.69
18	1	1	1	1	80.0	60	0.83	9	66.06	7.18
19	-1	-1	1	1	15.0	30	0.83	9	16.15	1.97
20	0	0	0	0	47.5	45	0.67	6	49.40	2.05
21	0	0	1	0	47.5	45	0.83	6	37.63	1.01
22	0	0	0	0	47.5	45	0.67	6	49.30	-0.88
23	0	-1	0	0	47.5	30	0.67	6	45.34	3.06
24	0	0	0	0	47.5	45	0.67	6	49.87	-0.31
25	1	0	0	0	80.0	45	0.67	6	54.95	-2.76
26	0	1	0	0	47.5	60	0.67	6	58.69	0.62
27	0	0	0	-1	47.5	45	0.67	3	47.45	1.12
28	0	0	-1	0	47.5	45	0.50	6	63.24	-0.50
29	0	0	0	1	47.5	45	0.67	9	52.93	-0.27
30	-1	0	0	0	15.0	45	0.67	6	43.80	1.15

*R-residual, $R = Y_{exp} - Y_{pred}$

Table S4: Experimental design matrix for EODS of DBT using [$P_{i444,1}$][Tos]

Run	Coded Values				Actual Values				%SR	
	X_1	X_2	X_3	X_4	X_1	X_2	X_3	X_4	Y_{exp}	R
1	0	0	0	0	47.5	45	0.67	6	87.60	0.78
2	1	-1	-1	-1	80.0	30	0.50	3	78.68	4.87
3	-1	-1	-1	1	15.0	30	0.50	9	60.29	-2.17
4	-1	1	1	1	15.0	60	0.83	9	71.79	-2.15
5	1	1	-1	1	80.0	60	0.50	9	100.00	-1.49
6	-1	-1	1	-1	15.0	30	0.83	3	35.11	2.76
7	1	1	1	-1	80.0	60	0.83	3	95.43	0.20
8	-1	1	-1	-1	15.0	60	0.50	3	74.52	-1.52
9	1	-1	1	1	80.0	30	0.83	9	64.10	-1.98
10	0	0	0	0	47.5	45	0.67	6	87.51	0.69
11	1	1	-1	-1	80.0	60	0.50	3	90.15	0.55
12	0	0	0	0	47.5	45	0.67	6	87.99	0.36
13	-1	-1	-1	-1	15.0	30	0.50	3	50.80	0.23
14	-1	1	-1	1	15.0	60	0.50	9	95.28	5.75
15	1	-1	1	-1	80.0	30	0.83	3	62.92	-2.50
16	1	-1	-1	1	80.0	30	0.50	9	85.99	-1.31
17	-1	1	1	-1	15.0	60	0.83	3	71.69	-1.59
18	1	1	1	1	80.0	60	0.83	9	99.08	1.57
19	-1	-1	1	1	15.0	30	0.83	9	30.93	-1.90
20	0	0	0	0	47.5	45	0.67	6	86.46	-1.16
21	0	0	1	0	47.5	45	0.83	6	88.05	4.69
22	0	0	0	0	47.5	45	0.67	6	88.10	-1.26
23	0	-1	0	0	47.5	30	0.67	6	72.98	2.10
24	0	0	0	0	47.5	45	0.67	6	89.40	0.04
25	1	0	0	0	80.0	45	0.67	6	94.93	0.11
26	0	1	0	0	47.5	60	0.67	6	98.00	-1.33
27	0	0	0	-1	47.5	45	0.67	3	78.95	-3.00
28	0	0	-1	0	47.5	45	0.50	6	89.55	-5.81
29	0	0	0	1	47.5	45	0.67	9	93.05	3.67
30	-1	0	0	0	15.0	45	0.67	6	72.31	0.89

R-residual, $Y_{pred} = Y_{exp} - R$

Table S5: ANOVA table for EODS of BT using $[P_{i444,1}][Tos]$

Source	SS^b	DF^b	MS^b	F^b Value	p-value Prob > F
Block	43.19	2	21.59		
Model	5824.35	7	832.05	45.32	< 0.0001
X_1	1015.20	1	1015.2	55.29	< 0.0001
X_2	1121.03	1	1121.03	61.06	< 0.0001
X_3	3307.59	1	3307.59	180.15	< 0.0001
X_4	133.73	1	133.73	7.28	0.0138
$X_1 X_4$	65.72	1	65.72	3.58	0.0731
$X_2 X_3$	85.98	1	85.98	4.68	0.0427
$X_2 X_4$	105.76	1	105.76	5.76	0.0262
Residual	367.21	20	18.36		
Lack of Fit	367.01	17	21.59	314.57	0.0003
Pure Error	0.2059	3	0.0686		
Cor Total	6234.75	29			

[a]R^2 = 94.11%, R^2(adj) = 91.99%, R^2(pred)=78.81%. [b]SS: Sum of square, DF: Degree of freedom of different source, MS: Mean of square, F: Degree of freedom, P: Probability

Table S6: ANOVA table for the EODS of DBT using $[P_{i444,1}][Tos]$

Source	SS^b	DF^b	MS^b	F^b Value	p-value Prob > F
Block	766.20	2	383.10		
Model	8145.41	11	740.49	63.03	< 0.0001
X_1	2448.18	1	2448.18	208.38	< 0.0001
X_2	3641.34	1	3641.34	309.93	< 0.0001
X_3	647.24	1	647.24	55.09	< 0.0001
X_4	225.36	1	225.36	19.18	0.0005
$X_1 X_2$	126.46	1	126.46	10.76	0.0047
$X_1 X_3$	99.44	1	99.44	8.46	0.0102
$X_2 X_3$	244.35	1	244.35	20.80	0.0003
$X_3 X_4$	125.83	1	125.83	10.71	0.0048
X_1^2	106.23	1	106.23	9.04	0.0084
X_2^2	49.68	1	49.68	4.23	0.0564
X_4^2	41.15	1	41.15	3.50	0.0797
Residual	187.98	16	11.75		
Lack of Fit	185.97	13	14.31	21.32	0.0141
Pure Error	2.01	3	0.6709		
Cor Total	9099.59	29			

[a]R^2 = 97.93%, R^2(adj) = 96.19%, R^2(pred)=90.73%. [b]SS: Sum of square, DF: Degree of freedom of different source, MS: Mean of square, F: Degree of freedom, P: Probability

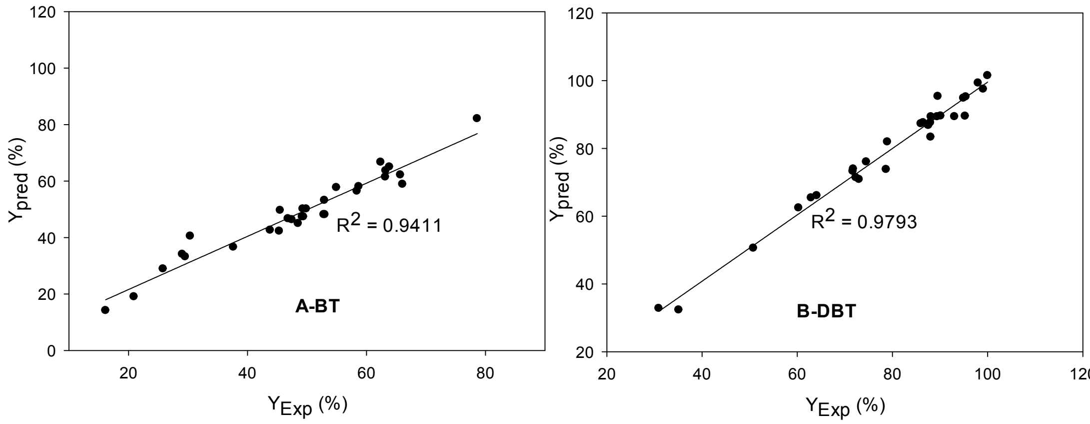

Figure S6: A plot of predicted response against experimental response for EODS of A-BT and B-DBT using [$P_{i444,1}$][Tos]

Optimization of the EODS of simulated fuel using [$P_{i444,1}$][Tos])

Table S7 presents the experimental design matrix for the OEDS of BT using the [$P_{i444,1}$][Tos] IL. Thirty experimental runs were carried out and the responses were fitted to a quadratic model. Table S8 shows the ANOVA of the EODS of BT using the [$P_{i444,1}$][Tos] IL. The model was found to be significant with an F-value of ~83 and p-value of < 0.01%. All independent variables possess significant effect on the efficiency of the process. Furthermore, temperature is the most significant variable (F value ≈ 267). Interestingly, mass fraction is the least significant with F value of ~19. According to the assumption made earlier, this means the %SR is no longer limited significantly by mass transfer and therefore a high %SR as compared to EODS strategy should be expected. Other significant terms include time-temperature, mass fraction-O/S and the second order term of time. The model, adjusted and predicted R^2 were found to be 0.9678, 0.9552 and 0.9102 respectively. Finally, Figure S7 shows a plot of the experimental response against the predicted response for this experiment.

Table S7: Experimental design matrix for OEDS of BT using [$P_{i444,1}$][Tos]

Run	Coded Values				Actual Values				%SR	
	X_1	X_2	X_3	X_4	X_1	X_2	X_3	X_4	Y_{exp}	R*
1	0	0	0	0	48.0	45	0.67	6	34.52	-5.23
2	1	-1	-1	-1	81.0	30	0.50	3	73.38	-3.10
3	-1	-1	-1	1	15.0	30	0.50	9	97.41	-3.71
4	-1	1	1	1	15.0	60	0.83	9	56.90	0.28
5	1	1	-1	1	81.0	60	0.50	9	72.98	2.22
6	-1	-1	1	-1	15.0	30	0.83	3	71.74	0.37
7	1	1	1	-1	81.0	60	0.83	3	15.04	5.66
8	-1	1	-1	-1	15.0	60	0.50	3	73.10	1.74
9	1	-1	1	1	81.0	30	0.83	9	65.40	0.81
10	0	0	0	0	48.0	45	0.67	6	69.46	0.95
11	1	1	-1	-1	81.0	60	0.50	3	85.96	-0.07
12	0	0	0	0	48.0	45	0.67	6	97.10	-0.82
13	-1	-1	-1	-1	15.0	30	0.50	3	48.65	-1.62
14	-1	1	-1	1	15.0	60	0.50	9	33.98	-2.57
15	1	-1	1	-1	81.0	30	0.83	3	84.32	3.68
16	1	-1	-1	1	81.0	30	0.50	9	25.18	0.52
17	-1	1	1	-1	15.0	60	0.83	3	76.75	4.92
18	1	1	1	1	81.0	60	0.83	9	72.78	0.94
19	-1	-1	1	1	15.0	30	0.83	9	78.07	5.41
20	0	0	0	0	48.0	45	0.67	6	31.91	-10.40
21	0	0	1	0	48.0	45	0.83	6	73.79	1.01
22	0	0	0	0	48.0	45	0.67	6	59.14	-3.08
23	0	-1	0	0	48.0	30	0.67	6	81.79	6.12
24	0	0	0	0	48.0	45	0.67	6	70.44	-6.96
25	1	0	0	0	81.0	45	0.67	6	71.52	-1.25
26	0	1	0	0	48.0	60	0.67	6	55.92	0.48
27	0	0	0	-1	48.0	45	0.67	3	83.05	-0.29
28	0	0	-1	0	48.0	45	0.50	6	50.81	1.84
29	0	0	0	1	48.0	45	0.67	9	72.57	4.41
30	-1	0	0	0	15.0	45	0.67	6	87.81	-2.30

*R-residual, R = Y_{exp}- Y_{pred}

Table S8: ANOVA for the OEDS of BT using [$P_{i444,1}$][Tos]

Source	SS^b	DF^b	MS^b	F^b Value	p-value Prob > F
Block	371.29	2	185.64		
Model	11790.28	7	1684.33	83.20	< 0.0001
X_1	3208.02	1	3208.02	158.46	< 0.0001
X_2	5409.23	1	5409.24	267.19	< 0.0001
X_3	383.79	1	383.79	18.96	0.0003
X_4	2008.62	1	2008.62	99.22	< 0.0001
$X_1 X_2$	131.78	1	131.78	6.51	0.0190
$X_3 X_4$	123.53	1	123.53	6.10	0.0226
X_1^2	525.30	1	525.30	25.95	< 0.0001
Residual	404.90	20	20.24		
Lack of Fit	393.49	17	23.15	6.09	0.0810
Pure Error	11.40	3	3.80		
Cor Total	12566.47	29			

[a]R^2 = 96.78%, R^2(adj) = 95.52%, R^2(pred)=91.02%. [b]SS: Sum of square, DF: Degree of freedom of different source, MS: Mean of square, F: Degree of freedom, P: Probability

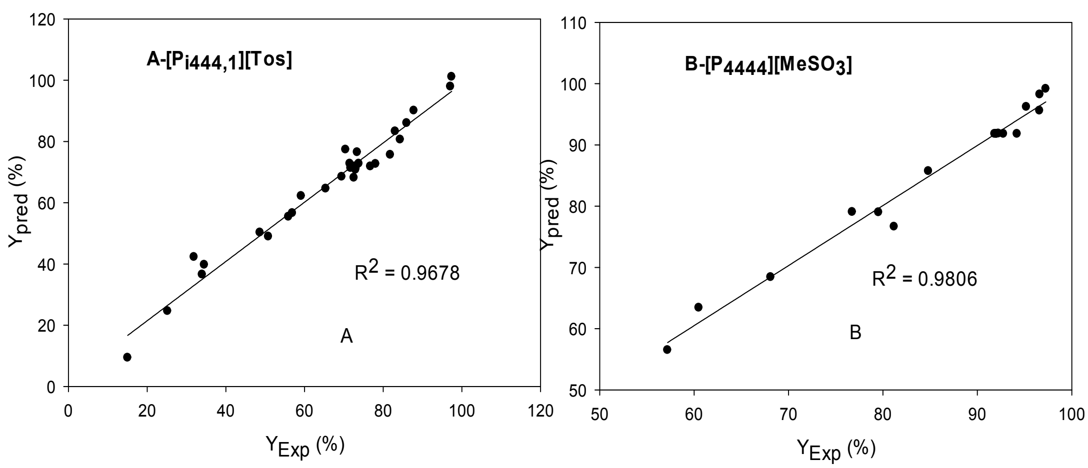

Figure S7: A plot of predicted response against experimental response for EODS of A-[$P_{i444,1}$][Tos], B-[P_{4444}][$MeSO_3$]

Optimization of the EODS of simulated fuel using [P_{4444}][$MeSO_3$])

The ANOVA table of the OEDS of BT using [P4444][$MeSO_3$] is presented as Table S10. The model is significant with F value of ~65. All the independent variables considered are significant with time as the most significant (F value of ~178) and mass fraction as by far the least significant factor (F value ≈ 33). Time-mass fraction and mass fraction-O/S are the only significant interaction terms. Second order terms of time and O/S are also significant. The model, adjusted and predicted R^2 were determined as 0.9806, 0.9654 and 0.8924 respectively.

Table S9: Experimental design matrix for the OEDS of BT using the $[P_{4444}][MeSO_3]$ IL

Run	Coded values			Actual values			%SR	
	X_1	X_2	X_3	X_1	X_2	X_3	Y_{exp}	R
1	1	-1	0	81	0.50	6	96.59	1.00
2	0	0	0	48	0.67	6	94.20	2.40
3	-1	0	1	15	0.67	9	81.19	4.54
4	0	-1	1	48	0.5	9	96.61	-1.63
5	0	0	0	48	0.67	6	92.05	0.26
6	0	1	1	48	0.83	9	95.19	-1.01
7	-1	-1	0	15	0.50	6	76.75	-2.30
8	-1	0	-1	15	0.67	3	57.19	0.68
9	0	-1	-1	48	0.50	3	84.81	-0.92
10	1	1	0	81	0.83	6	92.23	0.37
11	-1	1	0	15	0.83	6	60.50	-2.92
12	1	0	-1	81	0.67	3	79.53	0.53
13	0	0	0	48	0.67	6	91.84	0.04
14	1	0	1	81	0.67	9	97.25	-1.90
15	0	0	0	48	0.67	6	92.76	0.96
16	0	0	0	48	0.67	6	92.00	0.20
17	0	1	-1	48	0.83	3	68.11	-0.30

R-residual, $Y_{pred} = Y_{exp}$-R

Table S10: ANOVA for the OEDS of BT using the $[P_{4444}][MeSO_3]$

Source	SS[b]	DF[b]	MS[b]	F[b] Value	p-value Prob > F
Model	2584.58	7	369.23	64.80	< 0.0001
X_1	1011.57	1	1011.57	177.52	< 0.0001
X_3	187.45	1	187.45	32.90	0.0003
X_4	812.02	1	812.02	142.50	< 0.0001
$X_1 X_3$	35.37	1	35.37	6.21	0.0343
$X_3 X_4$	58.35	1	58.35	10.24	0.0108
X_1^2	366.55	1	366.55	64.33	< 0.0001
X_4^2	91.44	1	91.44	16.05	0.0031
Residual	51.28	9	5.70		
Lack of Fit	47.47	5	9.49	9.96	0.0224
Pure Error	3.81	4	0.95		
Cor Total	2635.86	16			

[a]R^2 = 98.06%, R^2(adj) = 96.54%, R^2(pred)=89.24%. [b]SS: Sum of square, DF: Degree of freedom of different source, MS: Mean of square, F: Degree of freedom, P: Probability

Table S11: Coefficients of the fitted quadratic model for the EODS/OEDS sulfur compounds using the respective ILs

	$[P_{i444,1}]$ [Tos] EODS		$[P_{i444,1}]$ [Tos] OEDS	$[P_{4444}]$ $[MeSO_3]$ OEDS
	BT	DBT	BT	BT
	48.56	87.93	71.99	91.80
X_1	7.54	11.70	13.35	11.24
X_2	7.89	14.23	17.34	
X_3	-13.56	-6.00	-4.62	-4.84
X_4	2.73	3.54	10.56	10.07
X_1X_2		-2.82	-2.87	
X_1X_3		2.50		2.97
X_1X_4	2.03			
X_2X_3	2.32	3.91		
X_2X_4	2.57			
X_3X_4		-2.80	2.78	3.82
X_1^2		-6.24	-10.46	-9.32
X_2^2		-4.26		
X_3^2				
X_4^2		-3.87		-4.65

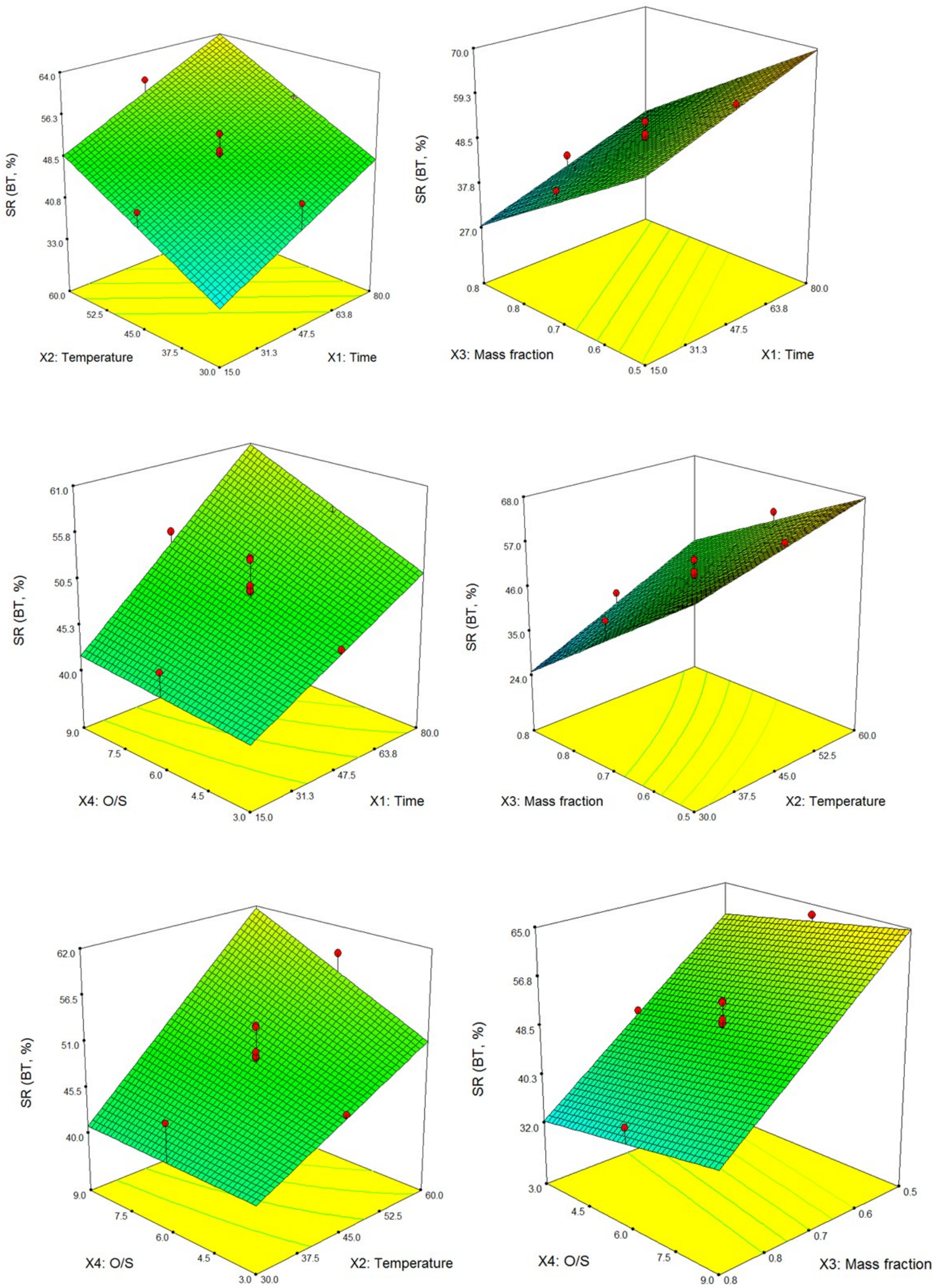

Figure S8: 3D plots for the EODS of BT using the $[P_{i444,1}][Tos]$

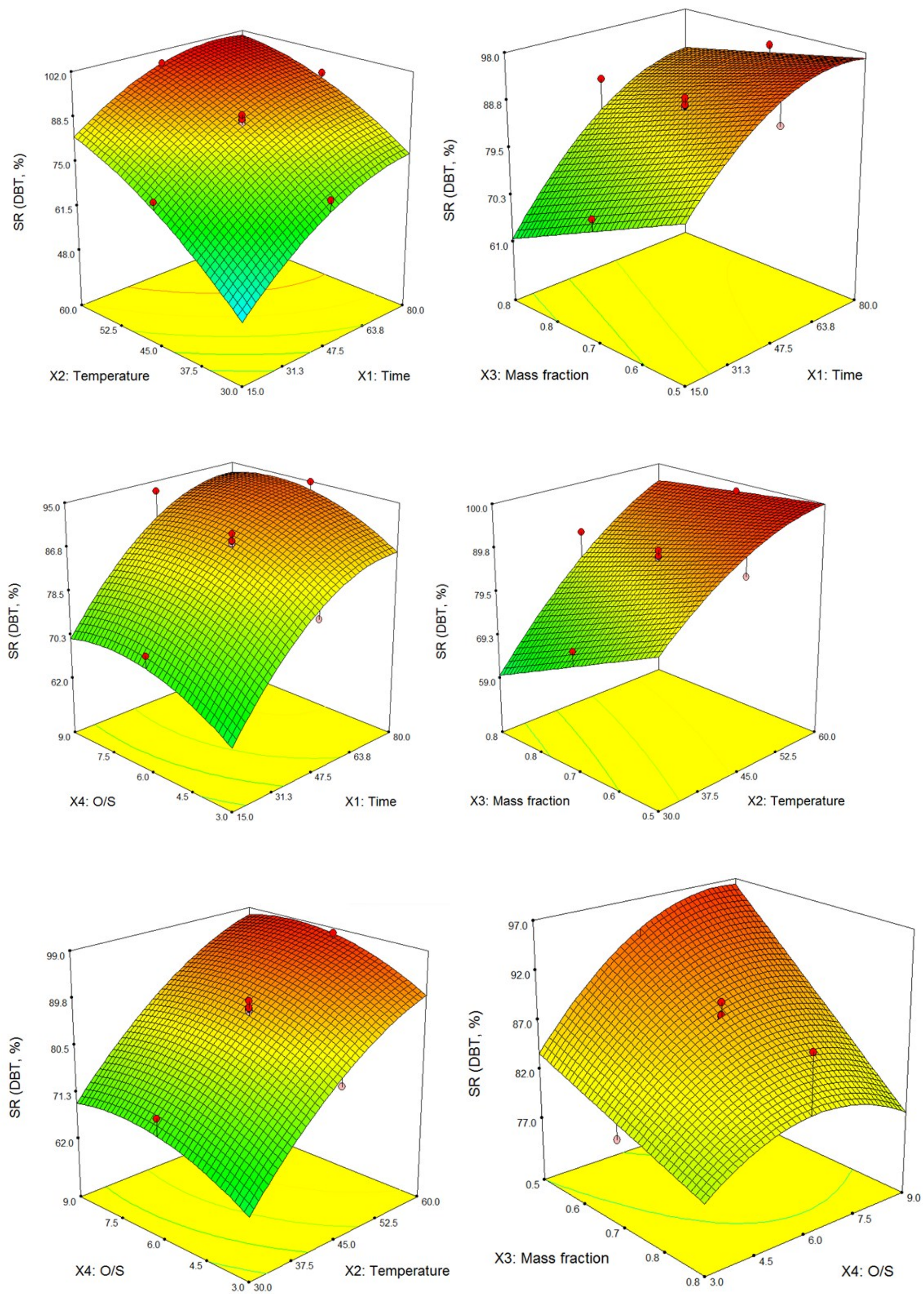

Figure S9: 3D plots for the EODS of DBT using the $[P_{i444,1}][Tos]$

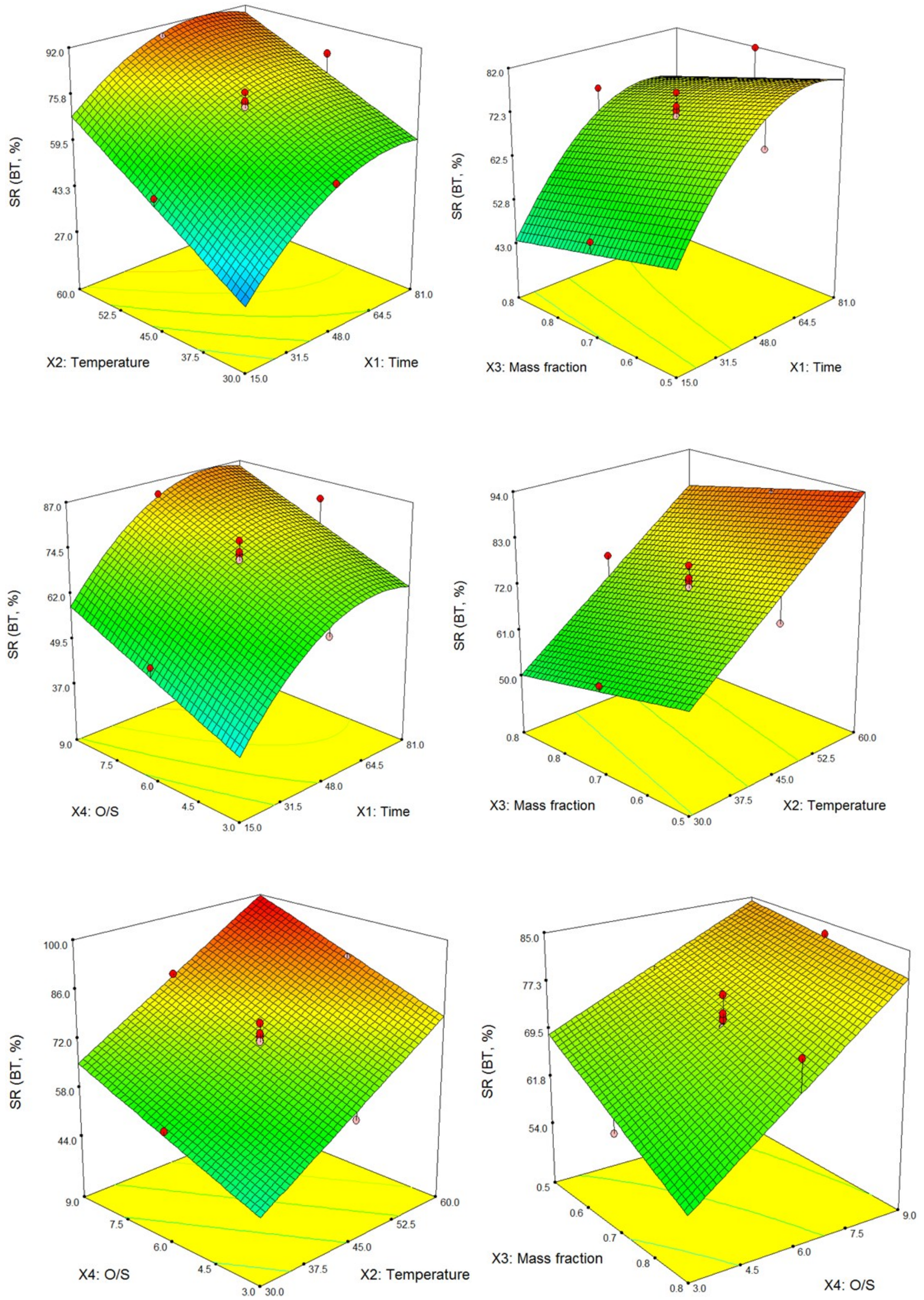

Figure S10: 3D plots for the OEDS of BT using the [$P_{i444,1}$][Tos]

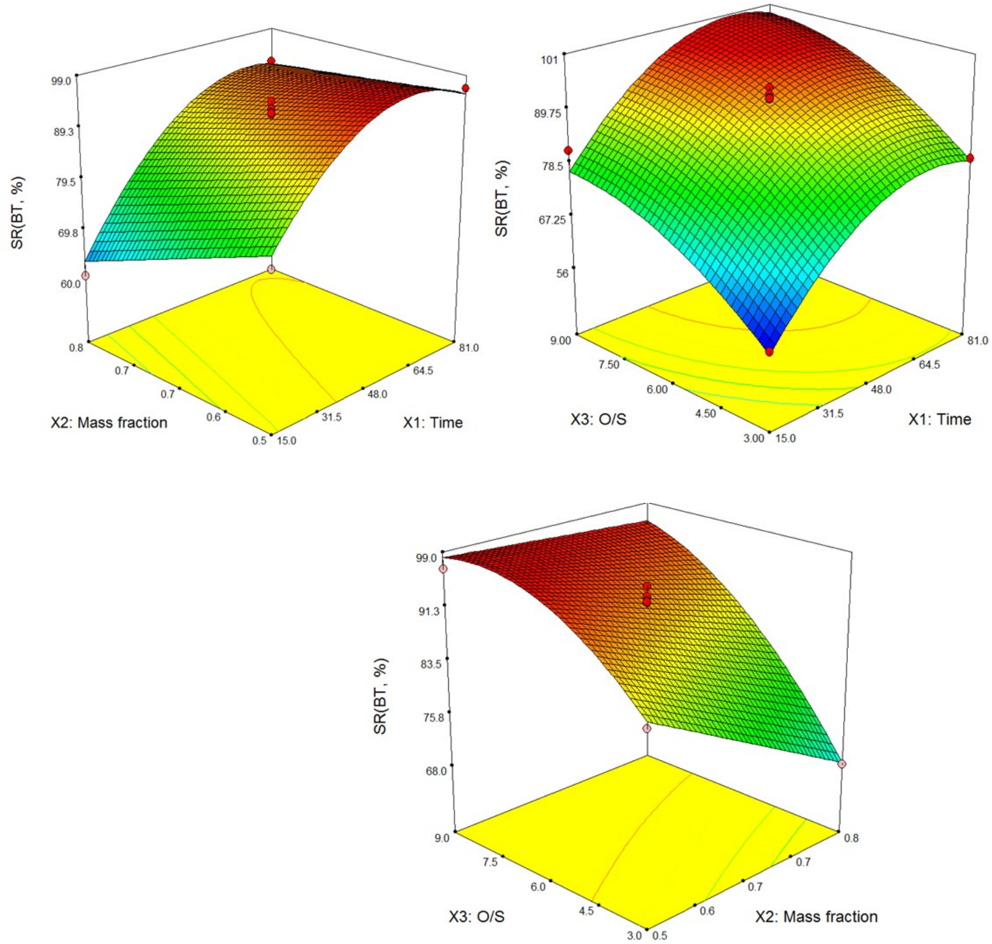

Figure S11: 3D plots for the OEDS of BT using the $[P_{4444}][MeSO_3]$