<u>Supplementary Material</u>: Experimental and Modeling Study on Autoignition of a Biodiesel/n-Heptane Mixture and Related Surrogate in a Heated Rapid Compression Machine

1. Description of the vector-based algorithm for optimal surrogate proportions

A novel algorithm was applied to determine the proportions of surrogate candidates, which is on the basis of calculation of Weighted Euclidean Distance (WED) in multidimensional vector space. In calculation of fuel proportions, ten parameters are taken into consideration, including carbon, hydrogen, oxygen numbers, H/C ratio and unsaturation degree, cetane number, density, low heat value, viscosity and molecular weight. Based on WED algorithm, each fuel parameter is defined as one dimension so that surrogate fuel with different compositions can be determined by a vector in multidimensional space. The distance between vectors is the metric in evaluation of surrogate fuels. The surrogate vector which is closest to target vector indicates the best performance in emulating properties of target fuels.

Taking the MO sub-surrogate as an example, the algorithm begins with vector $\vec{V}$ in a three-dimensional space, which represents the ratios of the ternary surrogates, respectively. Each element of vector $\vec{U}$ corresponds to one of the ten parameters of target and surrogate fuel. Matrix M is used to convert the three dimension vector $\vec{V}$ to the ten dimension linear Space Ω, which is shown in Equation 1.

$$\vec{U} = \vec{V} \cdot \mathrm{E} \cdot \mathrm{W} \cdot \mathrm{N} \qquad (1)$$

After multiplying $\vec{V}$ by matrix E, $\vec{V}$ is mapped onto a 10-dimensional linear space, which signifies the abovementioned 10 constraints on surrogate formulation. E denotes the Eigen matrix, which reflects the mixing rules of the constraints from individuals to entirety. W is the weighted square matrix and w1-w10 related to the contribution of each surrogate properties while N is defined as the normalization square matrix. Through analytic hierarchy process (AHP) analysis, matrix W can be expressed as Diag[0.149, 0.149, 0.149, 0.298, 0.447, 0.745, 0.149, 0.149, 0.149, 0.149], representing the 10 abovementioned constraints: carbon number, hydrogen number, oxygen number, H/C ratio, degree of non-saturation, cetane number, density, low heating value, viscosity, and molecular weight. Of these factors, cetane number has the largest weight coefficient.

Vector U_0 stands for the target fuel in the 10-dimensional space representing the 10 required molecular and combustion properties. The Euclidean distance between U and U_0 represents the degree of deviation between the surrogate and the target fuel. The optimal ratio of surrogate components can be found when the Euclidean distance takes its minimum value, as shown in Eq. (2), which can be solved using Matlab.

$$\exists x = x_0, y = y_0, z = z_0, \|\vec{U} - \vec{U}_0\| = \mathrm{Min}(\mathrm{d}\langle \vec{U} - \vec{U}_0 \rangle) \qquad (2)$$

Based on the above matrix manipulations, optimal surrogate for MP, MS, MO, ML and MLE are shown in Table 1 in the manuscript.

	Methyl decanoate	**Methyl trans-3-hexenoate**	**N-hexadecane**	**1, 4-hexadiene**
Methyl palmitate	59.51%	\	40.49%	\
Methyl stearate	47.77%	\	52.23%	\
Methyl oleate	61.06%	23.85%	15.09%	\
Methyl linoleate	65.79%	\	5.00%	29.21%
Methyl linolenate	57.63%	\	7.15%	35.22%

Table S1. Surrogate components and proportions for methyl esters.

2. Ignition delay data in RCM.

Test 1: Ignition delays of SME30					
ϕ	P_C (bar)	T_C (K)	1000/TC	Total ignition delay (ms)	First-stage ignition delay (ms)
0.6	14.99	641.3	1.5593600	121.6	54.72
0.6	15.01	641.5	1.5589300	120.1	54.06
0.6	15.01	657.8	1.5202100	84.72	29.32
0.6	15.03	658.0	1.5197800	84.02	29.34
0.6	15.05	672.7	1.4865100	62.52	16.32
0.6	15.03	672.7	1.4865800	67.44	19.02
0.6	15.04	672.8	1.4863800	63.86	18.12
0.6	15.02	687.7	1.4540400	45.68	10.34
0.6	15.00	687.5	1.4544400	45.94	12.64
0.6	14.99	687.5	1.4546400	45.26	9.98
0.6	14.94	687.0	1.4556400	45.80	10.56
0.6	14.94	701.9	1.4246100	35.26	5.34
0.6	15.00	701.9	1.4246400	35.26	5.12
0.6	15.05	702.3	1.4238700	35.30	5.30
0.6	15.01	718.9	1.3911000	30.70	2.52
0.6	15.02	719.0	1.3909100	30.88	2.18
0.6	15.03	736.8	1.3572900	28.54	1.56
0.6	15.00	736.5	1.3578400	29.50	1.90
0.6	15.00	754.1	1.3260400	30.82	1.10
0.6	15.00	754.1	1.3260400	30.50	1.02
0.6	15.08	772.3	1.2949000	32.94	1.58

Test 2: Ignition delays of WCOME30					
ϕ	P_C (bar)	T_C (K)	1000/TC	Total ignition delay (ms)	First-stage ignition delay (ms)
0.6	15.01	634.7	1.5755800	149.92	72.02
0.6	15.01	634.7	1.5755800	150.20	72.92
0.6	15.02	648.2	1.5427100	96.96	39.56
0.6	15.04	648.3	1.5424300	100.82	44.62
0.6	15.03	648.3	1.5425000	90.06	36.98
0.6	15.04	648.4	1.5422800	95.70	39.70
0.6	15.09	663.8	1.5065900	66.36	22.24
0.6	15.00	663.6	1.5068300	67.94	22.74
0.6	15.02	663.8	1.5065700	68.32	23.10
0.6	15.03	677.5	1.4759300	54.36	13.96
0.6	15.05	677.8	1.4753500	54.84	14.18
0.6	15.04	693.3	1.4424700	42.30	7.94
0.6	15.08	693.7	1.4414900	42.64	8.38
0.6	15.06	693.6	1.4416900	43.42	8.24
0.6	15.07	711.6	1.4053800	32.70	5.22
0.6	15.01	711.5	1.4054800	33.32	5.16
0.6	15.04	711.8	1.4049000	32.36	5.00
0.6	15.05	732.8	1.3647200	29.78	2.16
0.6	15.01	732.5	1.3652200	29.62	1.84
0.6	14.98	756.5	1.3218900	26.28	1.04
0.6	15.03	757.0	1.3210000	25.98	1.24
0.6	15.00	779.5	1.2829000	30.64	/

Test 3: Ignition delays of SME30 surrogate					
ϕ	P_C (bar)	T_C (K)	1000/TC	Total ignition delay (ms)	First-stage ignition delay (ms)
0.6	14.95	634.1	1.5769400	164.90	109.18
0.6	15.00	634.4	1.5763900	166.22	117.54
0.6	15.03	647.7	1.5438900	94.20	67.44
0.6	15.00	647.5	1.5443900	91.48	63.54
0.6	15.03	647.8	1.5437400	93.90	66.86
0.6	15.03	662.5	1.5093600	60.70	38.22
0.6	15.03	662.5	1.5093600	60.90	38.12
0.6	15.03	677.7	1.4756400	42.30	22.40
0.6	15.07	678.1	1.4746600	42.24	22.42
0.6	15.06	678.1	1.4746800	42.56	22.56
0.6	14.95	694.8	1.4393000	30.60	12.20
0.6	14.98	694.9	1.4390900	30.62	12.24
0.6	14.96	714.8	1.3990400	24.14	6.46
0.6	15.00	715.1	1.3985000	24.14	6.54
0.6	15.00	733.4	1.3635900	20.56	3.22
0.6	15.06	734.0	1.3624900	20.74	3.30
0.6	15.03	752.9	1.3281400	19.98	1.60
0.6	15.02	752.8	1.3283200	20.06	1.66
0.6	15.03	772.4	1.2946400	21.58	1.72
0.6	15.04	772.5	1.2944700	21.52	1.72
0.6	14.97	795.4	1.2572400	27.78	/
0.6	14.97	795.2	1.2575600	27.84	/

Test 4: Ignition delays of WCOME30 surrogate					
ϕ	P_C (bar)	T_C (K)	1000/TC	Total ignition delay (ms)	First-stage ignition delay (ms)
0.6	15.04	634.7	1.5755700	135.00	103.60
0.6	15.00	648.3	1.5424800	88.30	61.80
0.6	14.98	648.2	1.5427600	89.50	63.00
0.6	15.00	664.7	1.5044700	54.30	32.90
0.6	14.93	664.0	1.5059300	54.90	33.14
0.6	14.95	664.0	1.5060100	54.84	33.06
0.6	15.02	681.0	1.4684200	38.40	19.00
0.6	15.05	681.3	1.4678200	38.80	19.40
0.6	15.06	694.0	1.4408600	27.40	10.40
0.6	15.02	694.2	1.4405000	27.90	10.60
0.6	15.01	711.0	1.4064600	23.50	6.40
0.6	14.99	710.8	1.4068400	23.50	6.40
0.6	14.97	725.4	1.3785700	20.60	3.78
0.6	14.99	725.6	1.3781900	20.72	3.82
0.6	15.02	741.8	1.3481100	19.54	2.06
0.6	15.03	741.9	1.3479300	19.68	2.08
0.6	15.02	759.0	1.3175700	19.68	1.38
0.6	15.02	758.8	1.3178400	19.72	1.38
0.6	15.05	775.9	1.2888900	22.02	1.36
0.6	15.01	775.6	1.2892800	22.20	1.36

3. **Ignition delay data of pure surrogates at the equivalence ratio of 1.5.**

Test 5&6: Ignition delays of SME surrogate					
ϕ	P_C (bar)	T_C (K)	1000/TC	Total ignition delay (ms)	First-stage ignition delay (ms)
1.5	20.01	663.9	1.5063200	75.12	49.74
1.5	20.04	679.1	1.4726100	51.86	29.26
1.5	20.02	695.7	1.4374200	29.44	15.22
1.5	20.00	710.2	1.4079600	26.28	8.88
1.5	20.01	728.7	1.3723500	19.16	5.34
1.5	20.00	749.3	1.3344900	17.14	2.90
1.5	20.01	769.0	1.3004600	17.00	1.40
1.5	20.03	790.7	1.2646700	18.46	1.38
1.5	20.02	809.7	1.2350400	18.22	1.40
1.5	14.97	664.6	1.5045900	104.78	63.42
1.5	14.95	679.3	1.4722000	64.24	36.92
1.5	15.04	695.1	1.4385700	47.84	19.84
1.5	14.97	711.0	1.4064100	44.94	12.60
1.5	15.01	728.6	1.3724700	32.10	7.54
1.5	15.00	748.1	1.3367300	32.74	4.02
1.5	15.02	769.2	1.3000800	35.92	2.52
1.5	15.02	787.1	1.2704600	35.16	1.82
1.5	15.03	807.2	1.2388200	38.56	/
1.5	15.00	831.3	1.2030000	45.04	/

Test 7&8: Ignition delays of WCOME surrogate					
ϕ	P_C (bar)	T_C (K)	1000/TC	Total ignition delay (ms)	First-stage ignition delay (ms)
1.5	20.01	677.0	1.4771300	48.94	25.62
1.5	20.03	689.8	1.4497800	36.98	16.16
1.5	20.04	706.5	1.4153600	27.62	8.48
1.5	20.03	722.5	1.3841100	23.42	5.40
1.5	20.01	736.3	1.3581500	21.16	2.70
1.5	20.01	753.8	1.3266200	17.84	1.60
1.5	19.99	770.3	1.2981900	18.06	1.14
1.5	20.03	788.1	1.2688500	19.62	/
1.5	20.02	804.1	1.2435600	20.90	/
1.5	15.02	678.0	1.4748600	72.94	31.52
1.5	15.03	691.4	1.4463300	54.40	18.04
1.5	15.04	707.1	1.4142100	48.68	11.20
1.5	15.01	719.1	1.3906500	44.04	6.92
1.5	15.00	738.2	1.3547300	39.16	4.18
1.5	15.05	752.5	1.3288500	31.78	2.72
1.5	14.97	769.1	1.3003000	33.60	1.90
1.5	15.05	785.8	1.2725900	35.42	1.72
1.5	15.03	798.7	1.2520300	34.68	/