Supporting Information

Water and Methanol Cofeeding Modulate Kinetics in Crude-to-Chemicals Cracking

Isa Al Aslani[a,b], Juan Manuel Colom[a], Gontzal Lezcano[b], Arwa Alahmadi[a], Tuiana Shoinkhorova[a], Alla Dikhtiarenko[d], Mengmeng Cui[b], Lujain Alfilfil[c], Sultan Alsalman[c], Isidoro Morales Osorio[c], Khalid Almajnouni[c], Pedro Castaño[b,e]*, Jorge Gascon[a,e]*

[a] *Advanced Catalytic Materials, KAUST Catalysis Center (KCC), King Abdullah University of Science and Technology (KAUST), Thuwal, 23955-6900, Saudi Arabia.*

[b] *Multiscale Reaction Engineering, KAUST Catalysis Center (KCC), King Abdullah University of Science and Technology (KAUST), Thuwal, 23955-6900, Saudi Arabia.*

[c] *Sustainable Fuels & Chemicals Group, Aramco Research Center (ARC), Thuwal, 23955-6900, Saudi Arabia.*

[d] *Imaging and Characterization Department, KAUST Core Laboratories, King Abdullah University of Science and Technology (KAUST), Thuwal, 23955-6900, Saudi Arabia.*

[e] *Chemical Engineering Program, Physical Science and Engineering (PSE) Division, King Abdullah University of Science and Technology (KAUST), Thuwal, 23955-6900, Saudi Arabia.*

* Corresponding authors: pedro.castano@kaust.edu.sa, jorge.gascon@kaust.edu.sa

Set of rate equations used in the kinetic modeling, according to the reaction network and lumps 1-9 of Figure 1 (reactions taken from our previous work [42]).

(1) $d\bar{C}_1/dw = (\varepsilon_{cat} / q\rho_{cat})[\ \alpha_{31}k_{31}\bar{C}_3 + \alpha_{21}k_{21}\bar{C}_2 - (\alpha_{12}k_{12} + \alpha_{14}k_{14} + \alpha_{15}k_{15} + \alpha_{16}k_{16} + \alpha_{17}k_{17})\bar{C}_1\ ]$

(2) $d\bar{C}_2/dw = (\varepsilon_{cat} / q\rho_{cat})[\ \alpha_{32}k_{32}\bar{C}_3 + \alpha_{12}k_{12}\bar{C}_1 - (\alpha_{23}k_{23} + \alpha_{21}k_{21} + \alpha_{24}k_{24} + \alpha_{25}k_{25} + \alpha_{26}k_{26} + \alpha_{27}k_{27})\bar{C}_2\ ]$

(3) $d\bar{C}_3/dw = (\varepsilon_{cat} / q\rho_{cat})[\ \alpha_{23}k_{23}\bar{C}_2 - (\alpha_{38}k_{38} + \alpha_{32}k_{32} + \alpha_{31}k_{31} + \alpha_{34}k_{34} + \alpha_{35}k_{35} + \alpha_{36}k_{36} + \alpha_{37}k_{37})\bar{C}_3\ ]$

(4) $d\bar{C}_4/dw = (\varepsilon_{cat} / q\rho_{cat})[\ \alpha_{14}k_{14}\bar{C}_1 + \alpha_{24}k_{24}\bar{C}_2 + \alpha_{34}k_{34}\bar{C}_3\ ]$

(5) $d\bar{C}_5/dw = (\varepsilon_{cat} / q\rho_{cat})[\ \alpha_{15}k_{15}\bar{C}_1 + \alpha_{25}k_{25}\bar{C}_2 + \alpha_{35}k_{35}\bar{C}_3\ ]$

(6) $d\bar{C}_6/dw = (\varepsilon_{cat} / q\rho_{cat})[\ \alpha_{16}k_{16}\bar{C}_1 + \alpha_{26}k_{26}\bar{C}_2 + \alpha_{36}k_{36}\bar{C}_3\ ]$

(7) $d\bar{C}_7/dw = (\varepsilon_{cat} / q\rho_{cat})[\ \alpha_{17}k_{17}\bar{C}_1 + \alpha_{27}k_{27}\bar{C}_2 + \alpha_{37}k_{37}\bar{C}_3\ ]$

(8) $d\bar{C}_8/dw = (\varepsilon_{cat} / q\rho_{cat})[\ \alpha_{38}k_{38}\bar{C}_3\ ]$

where q is the total gas flow rate, ρ_{cat} denotes the bulk density of the catalyst, ε_{cat} indicates the packing fraction, C_i represents the average concentration of lump i over the entire time-on-stream, w denotes the weight of the catalyst, and α_j is the ratio of the molecular weight of the product divided by the molecular weight of the reactant.

The reaction rate constant k_{ij} follows the reparametrized Arrhenius equation: $k_{ij} = k_{0,ij} \exp[\ -E_{a,ij}/R\ (1/T-1/T_r)\ ]$ (9) where k0,ij and Ea,ij denote the rate constant at the reference temperature and apparent activation energy for the reaction between the i and j lumps, respectively. A reference temperature point T_r was set to 600 °C, as listed in Table 4, to facilitate the solving process. This temperature has been taken as it is the midpoint of the temperature range studied. An objective function was constructed to minimize the sum of the squared error between the experimental and calculated values to relate all kinetic parameters together. The number of significant kinetic pa rameters was reduced, keeping the statistical representativeness and the number of species or lumps of the model. The ode45 and lsqcurvefit routines in MATLAB were employed to solve the system of ordinary differential equations and obtain the kinetic parameters by minimizing the objective function. The 95 % confidence intervals were estimated using the nlparci routine and the corresponding estimation of the Jaco bian function evaluated at the optimal parameter estimates. Table S1 provides the input parameters in the model. The average molecular weights of the liquid lumps were estimated from Aspen HYSYS software after entering the required boiling range out of an inlet stream, defined by the built-in Arabian light petroleum assay, in the petroleum feeder unit operation and recording the molecular weight of the outlet stream. In contrast, butenes with pentenes and HC-lumps were assigned using the average molecular weights of the individual species. The molecular weight of coke was set to 750 g mol^{-1} , the middle value of the estimated region reported for asphaltene. Although the average molecular weights of the lumps vary during the reaction and depending on the cracking conditions, this shuttle difference in the molecular weight does not have an important effect on the model parameters.

Table S1. Input parameters in the model.

Parameter	Value
Bulk density of the catalyst (kg m^{-3})	765
Average packing porosity (m3 m^{-3})	0.57
Reference temperature point (°C)	600
Molecular weight (average in some cases)	
Gasoline (g mol^{-1})	115
Diesel (g mol^{-1})	224
Bottoms (g mol^{-1})	481
Ethylene (g mol^{-1})	28
Propylene (g mol^{-1})	42
Butenes + pentenes (g mol^{-1})	60
HC-lump (g mol^{-1})	30
Coke (g mol^{-1})	750

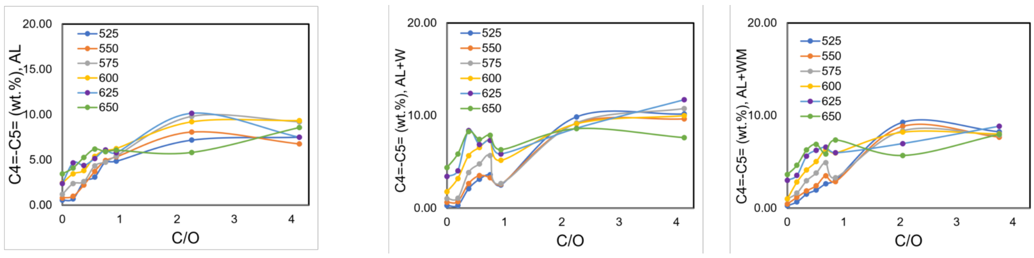

Figure S1: C4=+C5= lump yields for AL, AL+W(0.2) and AL+W(0.1)M(0.1)

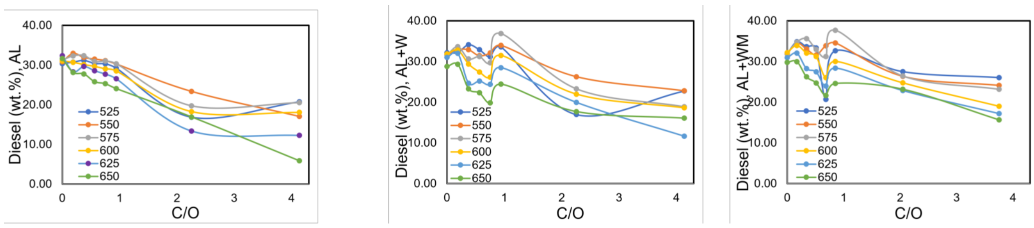

Figure S2: Diesel lump yields for AL, AL+W(0.2) and AL+W(0.1)M(0.1)

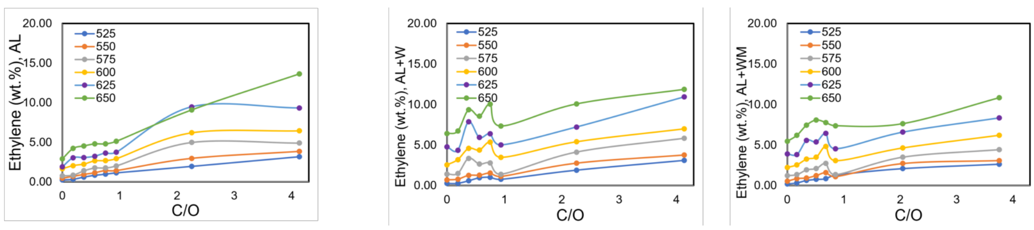

Figure S3: Ethylene lump yields for AL, AL+W(0.2) and AL+W(0.1)M(0.1)

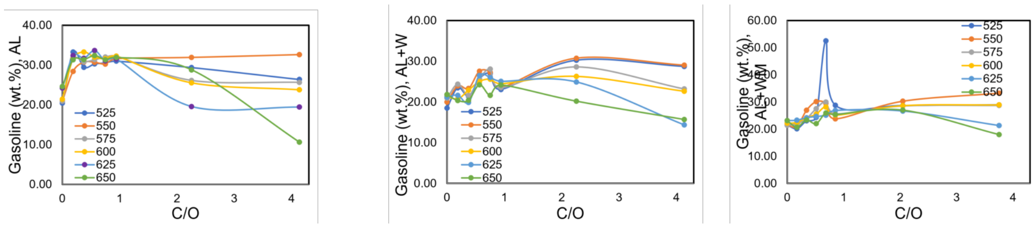

Figure S4: Gasoline lump yields for AL, AL+W(0.2) and AL+W(0.1)M(0.1)

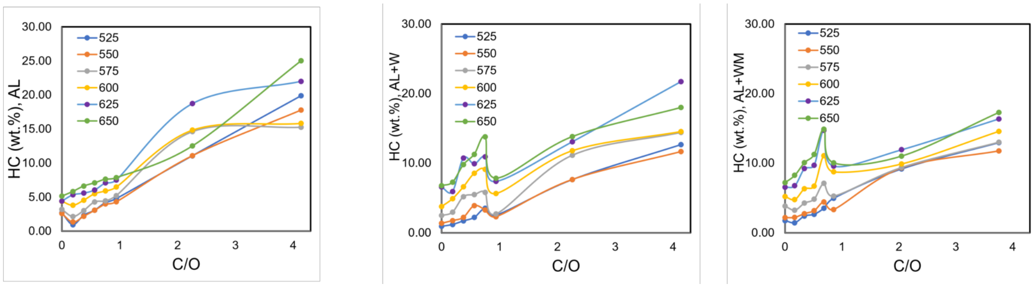

Figure S5: HC-lump yields for AL, AL+W(0.2) and AL+W(0.1)M(0.1)

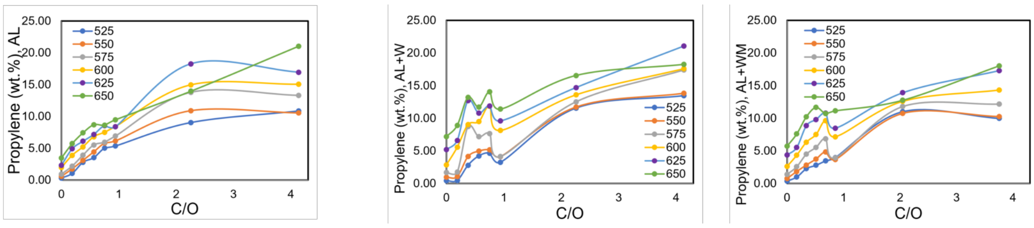

Figure S6: Propylene lump yields for AL, AL+W(0.2) and AL+W(0.1)M(0.1)

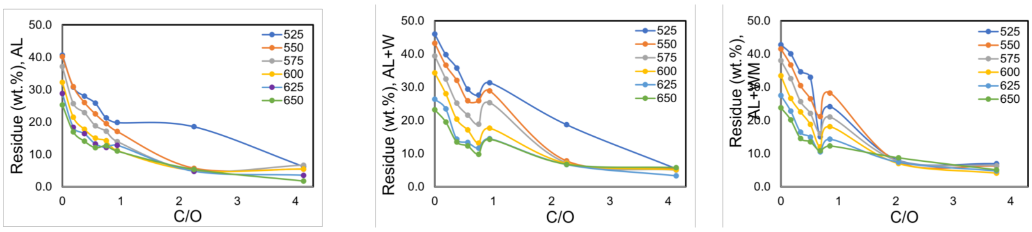

Figure S7: Bottoms lump yields for AL, AL+W(0.2) and AL+W(0.1)M(0.1)

Table S2: Raw data used in fitting the AL+W(0.2) kinetic model

C/O	Temp.	Coke	Bottoms	Diesel	Gasoline	$C_2^=$	$C_3^=$	$C_4^=$ $+C_5^=$	HC
-	°C	wt%	wt%	wt%	wt%	wt%	wt%	wt%	wt%
0.19	525	2.25	39.8	32.26	23.50	0.28	0.45	0.29	1.18
0.38	525	1.50	35.8	34.14	21.42	0.59	2.78	2.09	1.70
0.56	525	1.50	29.4	32.92	25.66	0.96	4.21	3.11	2.20
0.75	525	1.50	27.6	31.15	26.98	1.02	4.63	3.60	3.51
0.94	525	3.00	31.3	33.58	23.07	0.77	3.23	2.49	2.51
2.26	525	3.75	18.7	16.96	30.25	1.90	11.54	9.85	7.64
4.14	525	3.75	5.4	22.75	28.71	3.10	13.45	10.17	12.67
0.19	550	2.25	36.6	32.92	23.94	0.78	1.06	0.69	1.75
0.38	550	1.50	32.1	32.89	23.30	1.25	4.13	2.63	2.21
0.56	550	1.50	25.9	31.42	27.53	1.28	4.97	3.50	3.90
0.75	550	1.50	25.9	32.12	27.25	1.54	5.14	3.27	3.28
0.94	550	3.00	28.9	33.99	23.56	1.12	4.11	2.57	2.31
2.26	550	3.75	7.8	26.26	30.74	2.77	11.72	9.16	7.65
4.14	550	3.75	5.5	22.79	29.02	3.78	13.83	9.64	11.66
0.19	575	2.25	32.5	33.63	24.39	1.49	1.75	1.06	2.97
0.38	575	1.50	25.2	30.63	21.62	3.35	8.73	3.83	5.18
0.56	575	1.50	21.6	31.21	25.64	2.65	7.18	4.77	5.47
0.75	575	1.50	18.8	29.71	28.05	2.78	7.63	5.68	5.81
0.94	575	3.00	25.3	36.86	23.50	1.39	4.12	2.65	2.70
2.26	575	3.75	7.2	23.29	28.62	4.12	12.52	9.20	11.13
4.14	575	4.50	5.0	18.91	23.20	5.82	17.39	10.76	14.41
0.19	600	1.50	28.1	32.81	20.78	3.20	5.56	3.19	4.90
0.38	600	1.50	20.3	29.38	22.91	4.58	9.04	5.65	6.60
0.56	600	1.50	17.1	27.42	25.02	4.38	9.48	6.54	8.55
0.75	600	1.50	13.2	26.15	25.59	5.35	11.84	7.31	9.09
0.94	600	3.00	17.6	31.50	24.49	3.48	8.13	5.15	5.65
2.26	600	4.50	7.1	21.98	26.29	5.40	13.59	9.10	11.79
4.14	600	4.50	5.1	18.61	22.63	7.01	17.61	9.97	14.55
0.19	625	1.50	23.5	31.99	21.63	4.36	6.59	4.01	5.92
0.38	625	1.50	14.4	24.64	19.85	7.86	12.68	8.38	10.74
0.56	625	1.50	13.3	25.19	26.51	5.93	10.78	6.86	9.90
0.75	625	1.50	11.6	24.38	26.02	6.39	11.88	7.31	10.90
0.94	625	3.00	14.5	28.50	25.07	5.01	9.58	5.85	7.38
2.26	625	4.50	6.7	19.95	24.90	7.21	14.70	8.61	13.07
4.14	625	5.25	3.3	11.63	14.37	10.93	21.07	11.70	21.72
0.19	650	1.50	19.5	29.29	20.34	6.73	8.91	5.83	7.25
0.38	650	2.25	13.5	23.28	20.41	9.35	13.20	8.27	9.78
0.56	650	2.25	12.3	22.30	24.20	8.55	11.70	7.43	11.27
0.75	650	3.00	9.8	19.82	21.62	10.04	14.06	7.86	13.79
0.94	650	3.00	14.3	24.42	24.14	7.35	11.39	6.31	7.84
2.26	650	6.00	6.8	17.70	20.18	10.07	16.54	8.57	13.81
4.14	650	6.75	5.8	16.09	15.69	11.87	18.24	7.60	18.01