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## Water and methanol cofeeding modulates kinetics in crude-to-chemical cracking

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The co-processing of crude oil with green methanol offers a promising pathway for integrating renewable carbon into conventional refining, yet the presence of water or any hydrophilic components such as methanol can significantly influence catalyst performance, reaction selectivity, and overall process efficiency. We discuss experimental and kinetic modeling aspects of cofeeding water and methanol during crude oil catalytic cracking over a wide range of temperatures (525–650 °C) and catalyst-to-oil ratios (0–4.14) using a microactivity testing unit (MAT). During cofeeding, yields of gas and coke, and propylene-to-ethylene ratios fluctuated at low and high catalyst-to-oil ratios, respectively. Interestingly, cofeeding water and methanol lowered coke formation, while higher selectivity to light olefins over paraffins was observed in the presence of only water. Reparameterization of the kinetic model for Arabian light crude using water cofeeding data revealed changes in the intrinsic kinetic parameters of the cracking reactions. Specifically, the rate constant for the monomolecular cracking pathway leading to propylene increased across the entire temperature range, while the rate constants associated with condensation reactions, responsible for generating coke precursors, were reduced.

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### 1. Introduction

Blending crude oil with green methanol in co-processing schemes enables the introduction of renewable carbon into established refining operations. Understanding the effect of water is essential for interpreting methanol cofeeding behavior, as water, whether introduced with the methanol feed or produced during the reaction, can modify catalyst performance, influence product selectivity, and affect overall process efficiency. Notably, in direct crude-to-chemical conversion, deliberate water cofeeding has been reported to provide beneficial effects.<sup>1,2</sup> The cofeeding of water has been

proposed by previous studies in oil conversion processes due to several reasons: it is a cheap diluent and heat carrier,<sup>3–5</sup> feed atomizer,<sup>6</sup> hydrogen donor and coke gasifying agent,<sup>4,5,7,8</sup> promoter for monomolecular reactions leading to higher selectivity to light olefins<sup>4,5,7–9</sup> and sweeper for coke precursors from the catalyst surface.<sup>10,11</sup> On the other hand, methanol cofeeding<sup>12,13</sup> has been shown to increase the production of light olefins at low severity<sup>8</sup> and the production of carbon monoxide, carbon dioxide and alkylated benzenes at high severity.<sup>14–19</sup>

Care should be taken when comparing the impact of cofeeding on model compounds with markedly different chain lengths,<sup>20–23</sup> as such differences can lead to ambiguous or misleading interpretations. Corma *et al.* used *in situ* infrared spectroscopy to indicate that there is no interaction of water with the acid sites at typical cracking temperatures of *n*-hexadecane and hence it acts similarly to nitrogen,<sup>24</sup> whereas they concluded that water does interact with the active sites in *n*-heptane cracking leading to reversible deactivation.<sup>6</sup> Similarly, it was concluded by Corma *et al.* that there is no benefit in using steam when cracking hydrocarbon fractions that can be very easily evaporated.<sup>6</sup> In addition, Brait *et al.* reported that the water cofeeding effect on coke deposition in *n*-hexane cracking was insignificant while all reaction rates were lowered due to competitive

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adsorption.<sup>25</sup> Moreover, results from reactions in steel reactors might differ from quartz as iron oxides on the surface of steel reactors can be reduced during the reaction.<sup>26</sup> Cofeeding affects also catalyst stability and the type of deposited coke. Steam cofeeding produces irreversible dealumination<sup>3</sup> hence rare-earth metals,<sup>27</sup> phosphorus<sup>28</sup> and copper<sup>29</sup> can be incorporated to increase the stability of the zeolite framework, but can affect the acidic and basic properties.<sup>30</sup> Moreover, steam cofeeding leads to more aliphatic and less aromatic coke in crude oil cracking,<sup>10</sup> while the opposite was reported for *n*-hexane cracking.<sup>31</sup>

Kang *et al.*<sup>32</sup> explored a catalytic cracking process combining naphtha and methanol, where both substances undergo simultaneous cracking. During the study, it was discovered that optimizing the introduction points of naphtha and methanol in a circulating fluidized-bed reactor significantly enhances the yield of light olefins.<sup>32</sup> Pan *et al.*<sup>33–36</sup> found that methanol can improve the selectivity to light olefins during heavy oil fluid catalytic cracking, demonstrating its viability as a partial feedstock for this process.

Nowadays, novel strategies have emerged to boost the yields of both liquid products and light olefins through methanol cofeeding, such as the approach proposed by Yuan *et al.*,<sup>37</sup> involving continuous membrane emulsification. Moreover, Pan *et al.*<sup>33</sup> suggested that methanol should be fed before the oil at the bottom of the riser, which could be beneficial to the methanol conversion to light olefins. They concluded that feeding methanol at the bottom of the riser could enhance the heavy oil conversion in comparison with the maximum gas and diesel technology of fluid catalytic cracking. Similarly, it has been reported that, ideally, methanol should be mixed with the catalyst prior to blending with the oil to shield the catalyst from coke deposition at the beginning of the reaction, most likely due to the formation of steam during the conversion of the alcohol.<sup>33</sup>

Yan *et al.*<sup>38</sup> reported that the overall activation energy is lowered by cofeeding water and methanol in light naphtha catalytic cracking. Corma *et al.*<sup>24</sup> found that the adsorption equilibrium constant of water and nitrogen is much lower than that of *n*-hexadecane at temperatures higher than 400 °C. Moreover, *n*-hexadecane with cofeeding has a higher kinetic rate constant due to better contact between the feed and the catalyst<sup>24</sup> with an intersection between the slopes of with and without steam cofeeding over temperature for *n*-heptane cracking.<sup>6</sup> Other studies have proposed kinetic models with water cofeeding, but without a comparison with the no-cofeed case.<sup>39,40</sup>

On the other hand, a few studies have discussed the effect of cofeeding on the kinetic parameters. For example, Zhao *et al.* concluded that steam decreases the activation energies for all the elementary reactions in the catalytic cracking of 2-methylpentane.<sup>21</sup> Al-Shafei *et al.* found that steam cofeeding has decreased the activation energies and increased the reaction rate constants for all primary cracking reactions (except the reaction rate constant for the reaction leading to LPG) in steam catalytic cracking of *n*-dodecane.<sup>41</sup>

In a previous study from this group, we reported a kinetic model based on a simple but significant reaction network for the catalytic cracking of Arabian light crude oil covering wide ranges of temperature and catalyst-to-oil ratios.<sup>42</sup> In this work, we examined the influence of cofeeding in comparable temperature ranges and catalyst-to-oil ratios. For the case of water cofeeding, the kinetic parameters were reparameterized accordingly. The findings of this study provide a foundation for future multiphase simulations that incorporate deactivation and dilution effects.

## 2. Methodology

A micro-activity testing unit is used to investigate the catalytic cracking of Arabian light crude with water and methanol cofeeding using a physically mixed formulation consisting of two parent catalysts based on faujasite (FAU) and ZSM-5 zeolites.<sup>10</sup> Catalytic cracking experiments were performed with combinations of Arabian light, water and methanol in the temperature range from 525 °C to 650 °C and catalyst-to-oil ratio range of 0–4.14.

### 2.1 Catalyst

For the preparation of the catalysts, equal weights of two parent zeolites (P/ZSM-5 and faujasite) (Zeolyst) were physically mixed with kaolin clay (Sigma-Aldrich), 800 nm silicon carbide (US Research Nanomaterials), and an aluminum chlorohydrate binder (Al<sub>2</sub>(OH)<sub>5</sub>Cl) (Spectrum) to create the ACM-101-PM catalyst.<sup>10</sup> Following the slurry preparation, a laboratory-scale spray dryer was used to shape the spherical particles (comprising 38–100 μm (ref. 10)). It is worth mentioning that P/ZSM-5 refers to phosphorus-modified ZSM-5 zeolite. Phosphorus modification improves hydrothermal stability and reduces excessive acidity, which helps suppress undesired hydrogen transfer reactions and coke formation during cracking. Details are shown in Table 1.

To increase the catalyst's resistance to water dealumination during testing, the drying procedure was followed by calcination at 150 °C for one hour and steam treatment at 810 °C for seven hours (90% steam).

### 2.2 Experimental program

A total of 48 catalytic cracking experiments with Arabian light crude oil, matching the temperature range (525–650 °C) and catalyst-to-oil ratio range (0–4.14) reported in ref. 42, were repeated under two cofeeding conditions for direct comparison with the previous dataset: (i) 20 vol% water (AL + W(0.2)) and (ii) 10 vol% water with 10 vol% methanol (AL + W(0.1) + M(0.1)). In addition, several supplementary experiments were conducted to assess the influence of varying water and methanol contents (Table 2). Deionized water and methanol (99.9%, HPLC grade) were introduced *via* a separate syringe pump and combined with the crude oil stream in a T-shaped mixing joint prior to entering the



**Table 1** Composition of the ACM-101-PM catalyst and its two single-zeolite component systems<sup>10</sup>

Composition	Single-zeolite system (wt%)		ACM-101-PM after mixing (50 : 50 wt%)
	FAU-only	P/ZSM-5-only	
Kaolin clay	20	20	20
800 nm SiC additive	20	20	20
Faujasite zeolite (SAR = 30)	40	—	20
P/ZSM-5 (SAR = 23, P:Al = 0.4)	—	40	20
Al <sub>2</sub> O <sub>3</sub> binder	20	20	20

Notes: ACM: Advanced Catalytic Materials group, FAU: faujasite, SAR: silica to alumina molar ratio, PM: physically mixed, ZSM: Zeolite Socony Mobil.

**Table 2** Additional experiments to the full sets of AL + W(0.2) and AL + W(0.1) + M(0.1) varying the content of water and methanol performed at 625 °C

Experiment code	Water (vol%)	Methanol (vol%)	Hydrocarbon feed density (g ml <sup>-1</sup> )	C/O
AL + W(0.1)	10	0	0.866	0.940
AL + W(0.3)	30	0	0.866	0.940
AL + W(0.4)	40	0	0.866	0.940
AL + W(0.5)	50	0	0.866	0.940
AL + M(0.1)	0	10	0.859	0.853
AL + M(0.2)	0	20	0.851	0.765
AL + M(0.3)	0	30	0.844	0.675
AL + M(0.4)	0	40	0.836	0.583
AL + M(0.5)	0	50	0.829	0.490
AL + W(0.25) + M(0.25)	25	25	0.841	0.644
AL + W(0.33) + M(0.17)	33	17	0.848	0.722
AL + W(0.17) + M(0.33)	17	33	0.837	0.585

Notes: C/O: catalyst-to-oil ratio, AL: Arabian light, W: water, M: methanol.

reactor. Cofeeding kinetic parameters were determined by reparameterizing the previously established model using the new experimental data.

In each run, 1.33 g of oil was fed into the reactor over 75 s, after which any residual oil was purged from the catalyst bed using a nitrogen stream. Product gases were analyzed by gas chromatography (Thermo Scientific Trace 1310) equipped with one FID for hydrocarbon measurement and one TCD for N<sub>2</sub> and H<sub>2</sub> measurements. Coke formation was quantified by burning the spent catalyst at 720 °C and analyzing the evolved carbon species with an infrared analyzer.

### 2.3 Reaction network

The reaction network for the catalytic cracking of Arabian light crude oil was previously established using experimental data from a micro-activity testing (MAT) unit<sup>42</sup> (Fig. 1), and it has been adopted in the present work. In the previous study,<sup>42</sup> the cracking experiments were conducted at temperatures between 525 and 650 °C and catalyst-to-oil ratios from 0 to 4.14. Statistically significant reaction pathways were identified from the experimental results to define the reaction network. The hydrocarbon species were grouped into eight lumps based on chemical characteristics and boiling ranges: gas lumps (ethylene; propylene; butenes with pentenes; HC-lump comprising dry gases and other paraffins), liquid lumps (bottoms; diesel; gasoline), and coke. Interconversion between these lumps was

represented by forward first-order reactions, with backward reactions allowed among the liquid lumps. The optimal kinetic model, comprising nine reactions, was selected by minimizing both the number of significant kinetic parameters and the sum of squared errors between observed and predicted yields. Model robustness and applicability to other crude oil types were confirmed by validating the kinetic parameters against Arabian extra light crude oil. Although additional pathways could be included (*e.g.*, explicit methane or ethane formation), the present model focuses on dominant lump interconversions to avoid overparameterization. Minor gas products are included within the HC-lump, consistent with previous lumped FCC kinetic models. The final reaction network was selected by eliminating statistically insignificant reaction pathways while maintaining predictive accuracy. This reduced network minimized parameter uncertainty while preserving the dominant reaction pathways governing crude oil cracking.

The complete set of rate equations and parameter estimation procedure are given in our previous work<sup>42</sup> as well as in the SI of this study.

## 3. Results and discussion

### 3.1 Experimental data

Fig. 2 shows that water addition increases the propylene-to-ethylene ratio at 525 °C under both thermal and high catalyst-to-oil ratio conditions, as evidenced by the



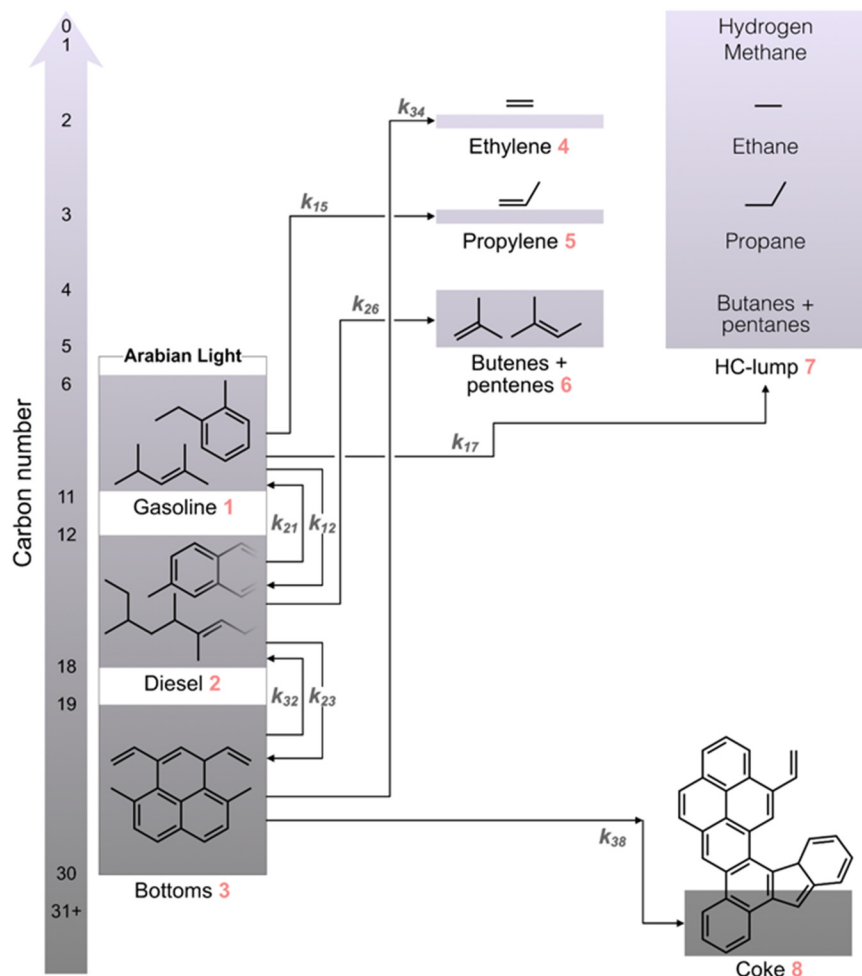


Fig. 1 Reaction network for the kinetic model.<sup>42</sup>

comparison between Fig. 2b (water cofeeding) and Fig. 2a (no cofeeding). Similarly, Fig. 2e demonstrates that water significantly reduces coke formation at high catalyst-to-oil ratios relative to Fig. 2d, while the combined cofeeding of methanol and water further suppresses coke yields (Fig. 2f). These observations are consistent with the catalyst surface cleaning effect previously proposed by Yan and Le Van Mao.<sup>12</sup>

Cofeeding water (Fig. 2h) or a water-methanol mixture (Fig. 2i) enhanced conversion, reflected in higher gas and coke yields, at low catalyst-to-oil ratios compared with the baseline case (Fig. 2g), primarily due to the promotion of monomolecular cracking reactions. At higher severities, however, the effect becomes negligible in some instances, consistent with the threshold proposed by Corma *et al.*, whereby the decline in conversion is offset once the catalyst-to-oil ratio reaches four, as sufficient active sites are available.<sup>43</sup>

Fig. 3 shows carbon monoxide, carbon dioxide, and hydrogen yields after cofeeding water and methanol. Methanol cofeeding produces higher amounts of carbon dioxide and hydrogen at lower temperatures, while it produces more carbon monoxide at higher temperatures, which agrees with the available data in the literature.<sup>44</sup> The second axis in Fig. 3(g-i)

illustrates that the increase in hydrogen yield is linked with the selectivity to paraffins over olefins. Therefore, it can be concluded that, within the high-temperature range examined in this study, methanol cofeeding does not improve olefin selectivity relative to paraffins.

Methanol cofeeding enhances isomerization reactions in both the gasoline fraction (Fig. 4a and e) and the gas phase (Fig. 4b and f) to a greater extent than water cofeeding alone under thermal cracking and most catalytic cracking conditions. At high temperature, methanol's contribution to increased isoparaffin formation becomes more pronounced at higher temperatures. This observed enhancement in isomerization products aligns with the findings of ref. 21, where water was shown to promote isomerization in 2-methylpentane cracking over ultra-stable Y zeolite at elevated temperatures with heavy feeds.

In Fig. 4c and g, combined water and methanol cofeeding increases the olefin-to-aromatic ratio under thermal conditions and at low catalyst-to-oil ratios. However, this effect diminishes in the remaining cases, likely due to the enhancement of aromatic production *via* hydrogen transfer reactions.<sup>10</sup> Furthermore, as illustrated in Fig. 4d and h, the



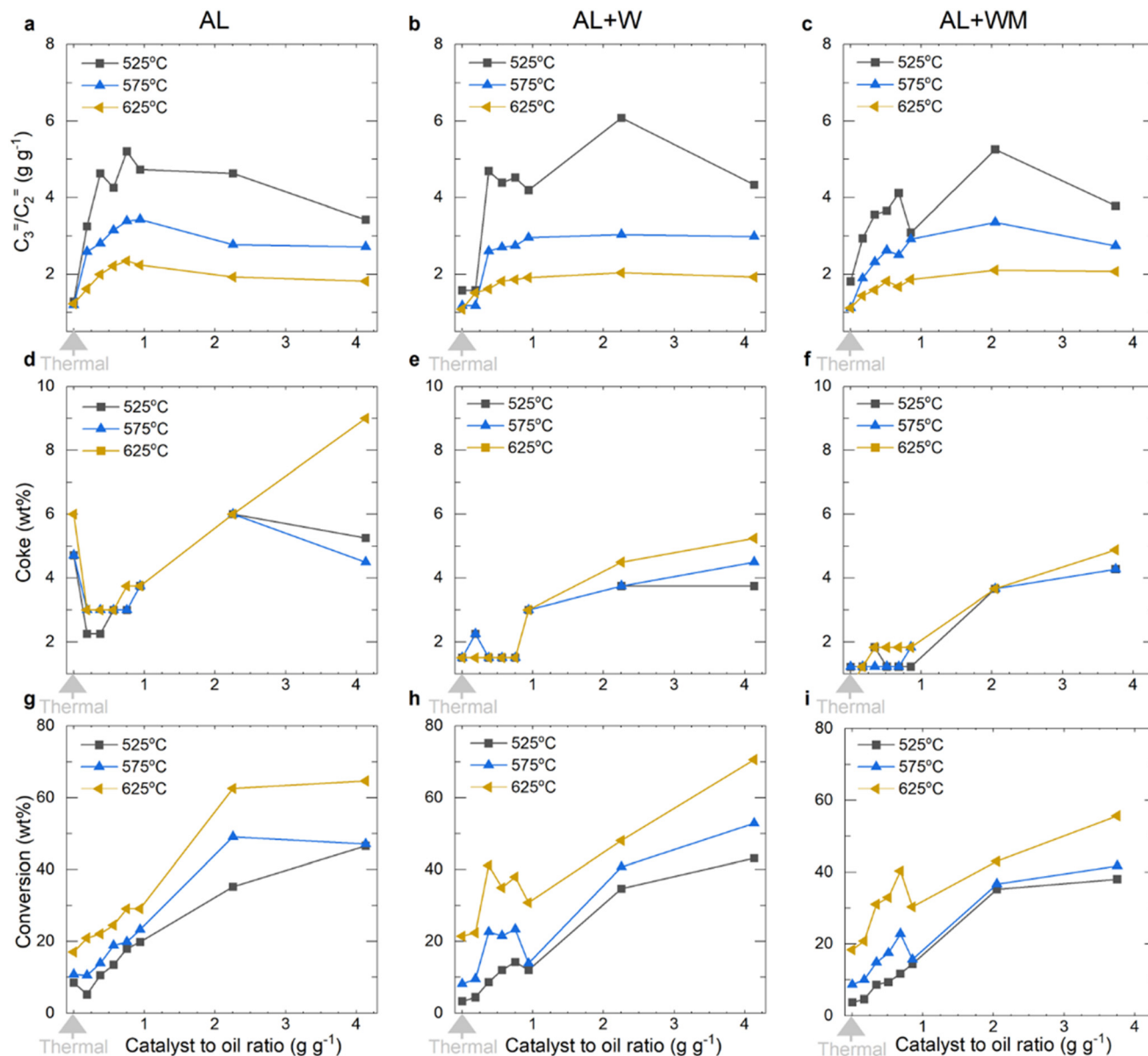


Fig. 2 Propylene to ethylene ratio (a–c), coke yield (d–f) and conversion (g–i) for AL, AL + W(0.2) and AL + W(0.1) + M(0.1) at different temperatures and catalyst-to-oil ratios.

introduction of water and methanol promotes the alkylation of benzene to toluene and xylenes at low temperatures and catalyst-to-oil ratios, an effect attributed to methyl radicals generated from methanol.<sup>14–17,19</sup>

Fig. 5a–d present additional experiments, which were conducted to evaluate the influence of varying water and methanol fractions on product distribution under fixed catalytic conditions (625 °C and 1.25 g catalyst). The objective was to identify trends in light olefin formation, coke production, and selectivity ratios as a function of cofeed composition. The highest light olefin yield, 30 wt%, was obtained at a composition of  $W = 0.4$  and  $M = 0$  (volume fractions), while the maximum propylene-to-ethylene ratio of 2.3 occurred at  $W = 0.33$  and  $M = 0.17$ . The light olefin yield peaked at 30 vol% methanol, in agreement with the findings of Yan *et al.*<sup>12</sup>

However, increasing methanol content also led to a pronounced rise in coke formation (Fig. 5c) and HC-lump production (Fig. 5d), accompanied by a relatively smaller increase in the light olefin yield (Fig. 5a), largely due to elevated methane production. These results reinforce the conclusion from the previous experiments that methanol cofeeding does not improve selectivity toward light olefins. Indeed, previous studies have reported that methanol cofeeding tends to favor methane formation over light olefins, particularly when catalyst activity is reduced by coke deposition.<sup>33</sup>

The effects of water and methanol cofeeding on thermal, monomolecular, and bimolecular reactions can be summarized as follows. In thermal reactions, water and methanol increase the propylene-to-ethylene ratio at 525 °C and markedly suppress coke formation. At 625 °C, they



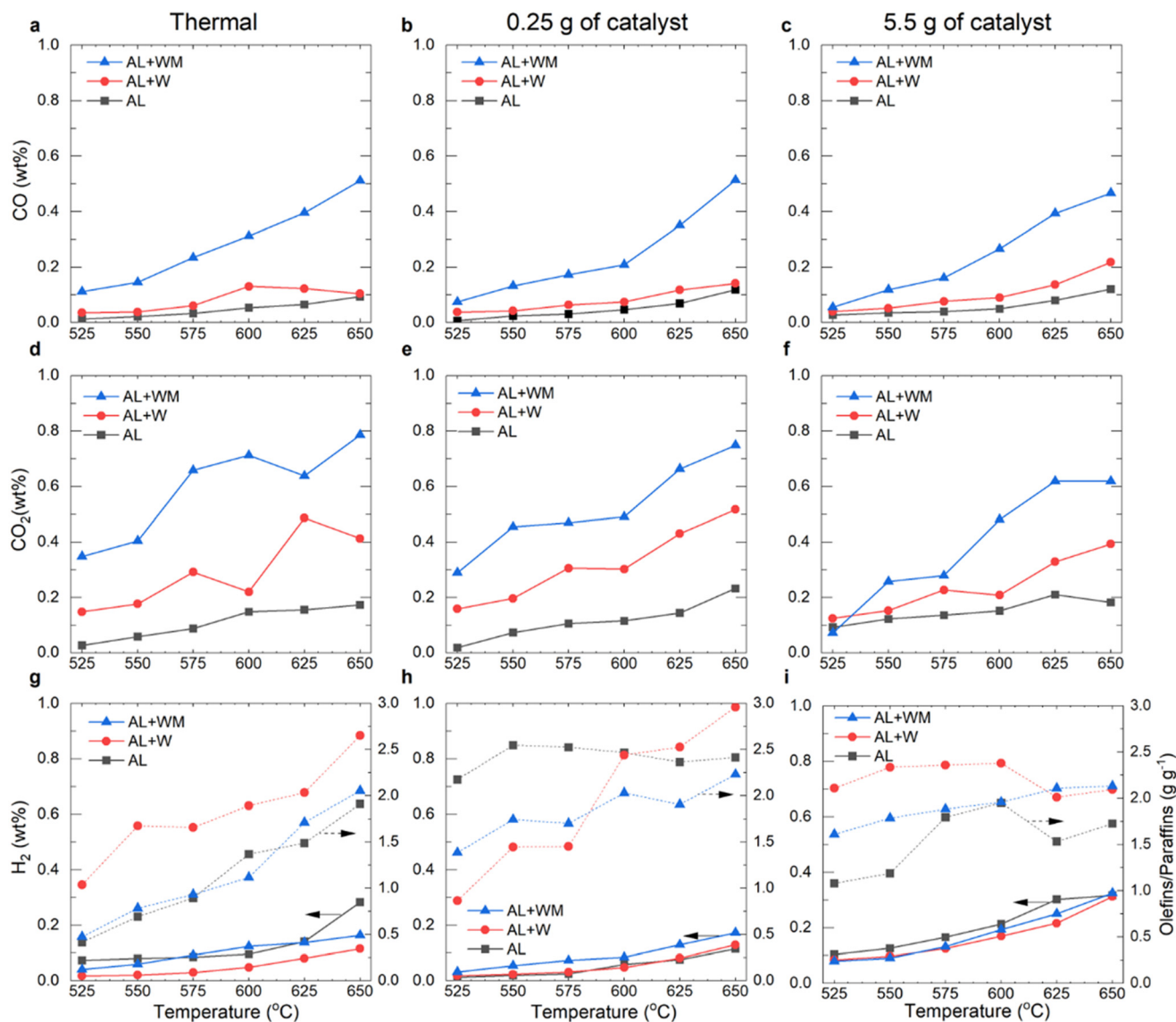


Fig. 3 Carbon monoxide (a–c), carbon dioxide (d–f) and hydrogen (g–i) for AL, AL + W(0.2) and AL + W(0.1) + M(0.1) at different temperatures and amounts of catalyst loading, as well as thermal conditions.

enhance conversion, raising CO, CO<sub>2</sub>, and the olefin-to-paraffin ratio, though the latter decreases when methanol is cofed with water. Both additives also promote isomerization in gas and liquid phases and increase the olefin-to-aromatic ratio in liquids under thermal conditions.

For monomolecular reactions, cofeeding particularly boosts conversion and propylene-to-ethylene ratios at low catalyst-to-oil ratios and higher temperatures. In bimolecular reactions, water and methanol significantly suppress coke formation at high catalyst loadings, thereby improving catalyst activity. Ethylene and propylene formation *via* oligomerization–cracking of butenes and pentenes is also observed (see SI figures). Overall, high-temperature thermal cracking remains critical due to its link with paraffin and syngas production, reflecting the complex interplay of reaction pathways reported in prior studies.

### 3.2 Kinetic model

Table 3 presents the fitted kinetic parameters obtained from the water cofeeding experiments, alongside the corresponding parameters from the no-cofeeding dataset for comparison.<sup>42</sup> Where  $E_{a,ij}$  is the apparent activation energy and  $k_{0,ij}$  is the rate constant at the reference temperature (600 °C), which was chosen as the midpoint of the temperature range studied and facilitates the solving process.<sup>42</sup>

The correlated variations in the kinetic parameters for all reactions, except diesel to bottoms, bottoms to coke, and bottoms to ethylene, can be attributed to changes in surface coverage induced by steam cofeeding.<sup>6</sup> The difference between forward and backward activation energies increased for the bottoms–diesel conversion (from –38 to –75 kJ mol<sup>–1</sup>) and decreased for the diesel–gasoline conversion (from –15



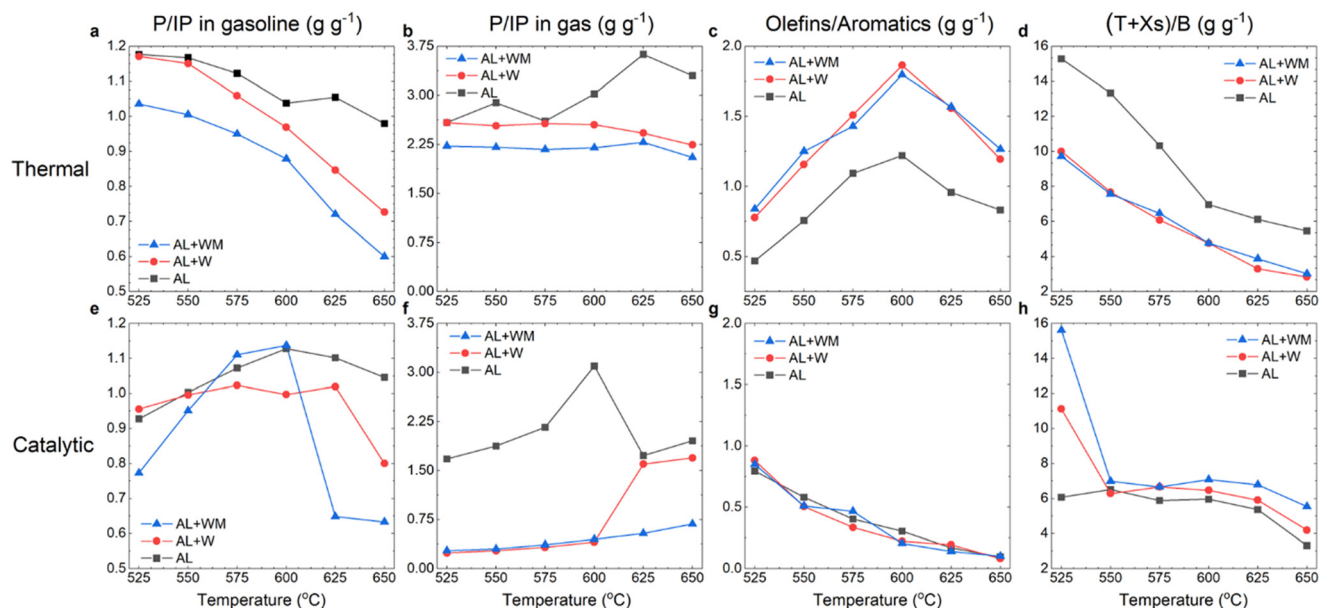


Fig. 4 Paraffin to isoparaffin ratio in gasoline (a and e) and gas (*n*-butane + *n*-pentane to *i*-butane + *i*-pentane) (b and f), olefins to aromatics in gasoline (c and g) and toluene + xylene to benzene ratio (d and h) for AL, AL + W(0.2) and AL + W(0.1) + M(0.1) at different temperatures under thermal and catalytic conditions, (e, f and g) = 5.5 g while h = 3 g.

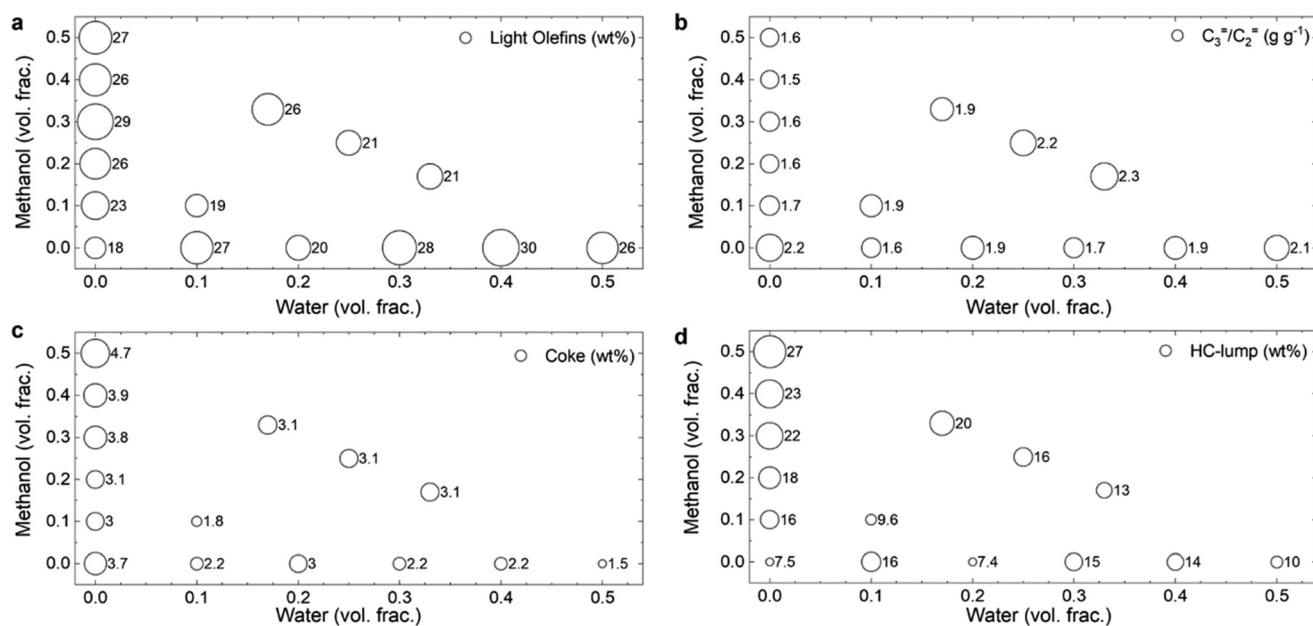


Fig. 5 Light olefins (a), yields and propylene to ethylene ratio (b), coke (c) and HC-lump (d) for several content values of methanol and water at a catalyst loading of 1.25 g and 625 °C.

to  $-2.7 \text{ kJ mol}^{-1}$ ). This suggests that water cofeeding promotes hydrogen transfer reactions in long-chain molecules ( $-85.5 \text{ kJ mol}^{-1}$ ) and isomerization reactions in short-chain molecules ( $-1.9 \text{ kJ mol}^{-1}$ ) over condensation pathways leading to coke precursors ( $-28.7 \text{ kJ mol}^{-1}$ ), as supported by density functional theory calculations.<sup>45</sup>

Fig. 6 shows the evaluated rate constants over the whole temperature range. Fig. 6h shows that cofeeding water increased the rate constant for the reaction to propylene at

the whole temperature range, which supports the fact that water enhances monomolecular cracking reactions.<sup>46</sup> In addition, the increasing effect of the other reactions occurs at certain temperature levels (similar intersections in the trends were reported by ref. 6) for the forward (Fig. 6e) and backward (Fig. 6f) gasoline to diesel, diesel to butenes with pentenes (Fig. 6g), and gasoline to HC-lump (Fig. 6i).

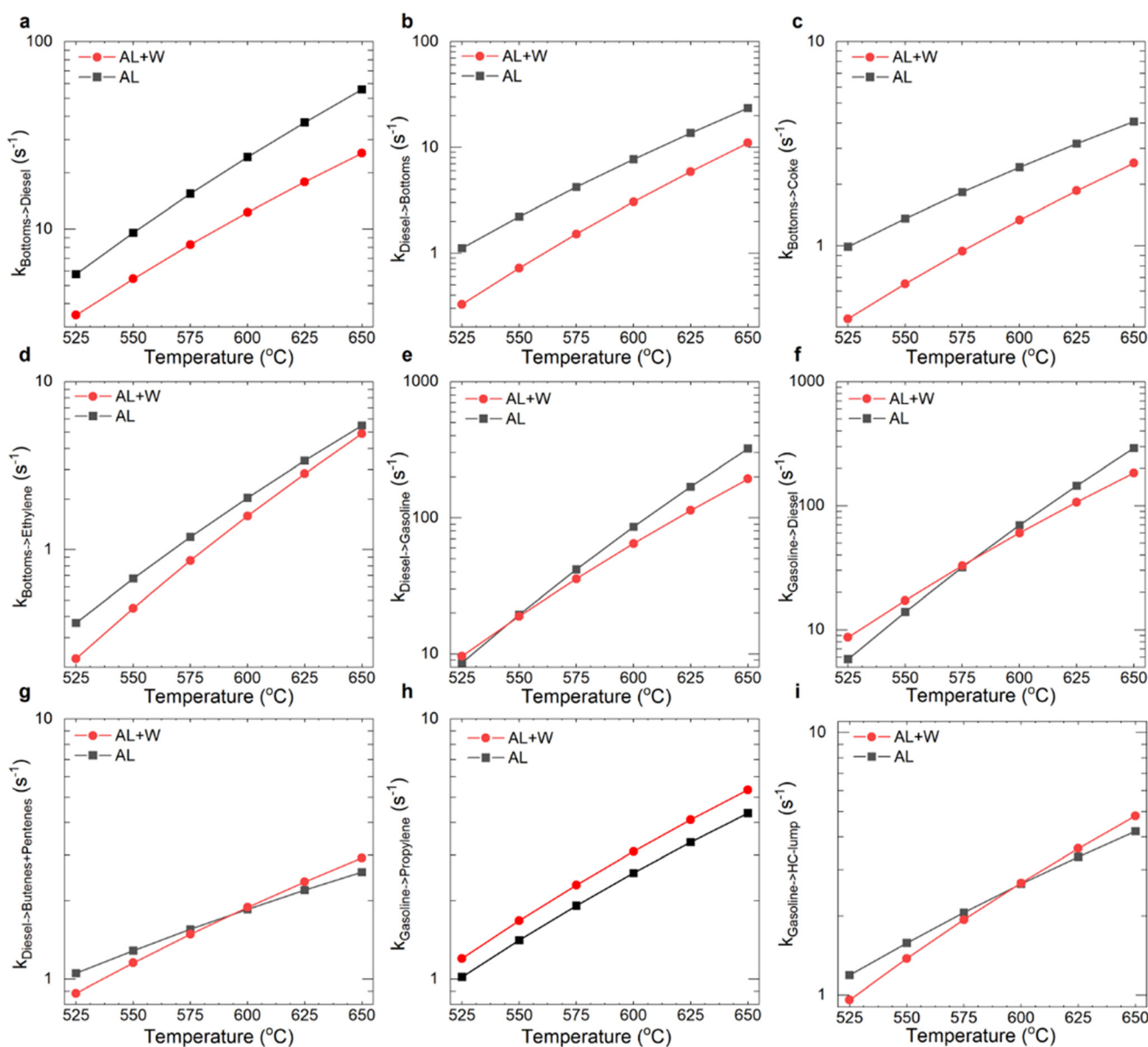
Because coke accumulates during MAT experiments, catalyst activity changes during the test. Therefore, the fitted



**Table 3** Kinetic parameters obtained with water cofeeding data compared with the no-cofeeding case,  $R^2 = 0.92$ 

Reaction	$k_{0,ij}$ ( $s^{-1}$ )		$E_{a,ij}$ ( $kJ\ mol^{-1}$ )	
	AL	AL + W	AL	AL + W
Bottoms to diesel ( $k_{32}$ )	23.2 ( $\pm 3.1$ )	12.3 ( $\pm 3.30$ )	111.2 ( $\pm 18.0$ )	97.5 ( $\pm 25.9$ )
Diesel to bottoms ( $k_{23}$ )	7.75 ( $\pm 1.90$ )	3.06 ( $\pm 2.39$ )	149.5 ( $\pm 35.7$ )	172.3 ( $\pm 81.2$ )
Bottoms to coke ( $k_{38}$ )	2.29 ( $\pm 0.35$ )	1.34 ( $\pm 0.38$ )	72.8 ( $\pm 20.5$ )	86.1 ( $\pm 41.5$ )
Bottoms to ethylene ( $k_{34}$ )	1.85 ( $\pm 0.35$ )	1.59 ( $\pm 0.47$ )	126.3 ( $\pm 30.6$ )	151.1 ( $\pm 47.4$ )
Diesel to gasoline ( $k_{21}$ )	85.9 ( $\pm 10.8$ )	64.7 ( $\pm 13.9$ )	177.4 ( $\pm 20.0$ )	146.9 ( $\pm 28.9$ )
Gasoline to diesel ( $k_{12}$ )	69.6 ( $\pm 10.1$ )	60.3 ( $\pm 13.3$ )	191.9 ( $\pm 23.9$ )	149.6 ( $\pm 30.0$ )
Diesel to butenes + pentenes ( $k_{26}$ )	1.77 ( $\pm 0.22$ )	1.89 ( $\pm 0.32$ )	46.2 ( $\pm 17.1$ )	58.7 ( $\pm 23.8$ )
Gasoline to propylene ( $k_{15}$ )	2.56 ( $\pm 0.25$ )	3.10 ( $\pm 0.41$ )	71.1 ( $\pm 14.1$ )	73.2 ( $\pm 19.6$ )
Gasoline to HC-lump ( $k_{17}$ )	2.52 ( $\pm 0.24$ )	2.67 ( $\pm 0.38$ )	61.9 ( $\pm 13.9$ )	79.1 ( $\pm 21.5$ )

Note: Values are given at a 95% confidence interval.

**Fig. 6** AL + W(0.2) and AL rate constants at the whole temperature range.

kinetic constants should be interpreted as effective parameters obtained from time-averaged product yields over the injection period, rather than intrinsic constants at a fixed catalyst state.<sup>42</sup>

Fig. 7 compares the experimental data for water cofeeding with the model predictions. Most deviations arise from the dominance of monomolecular cracking at low catalyst-to-oil ratios. While this low-ratio region is less relevant for practical fluid catalytic cracking (FCC) operation, where conversions are typically high, it remains important for developing a robust kinetic model with statistically significant parameters. The resulting model is suitable for integration into multiphase simulations, particularly once the limitations of using a micro-activity testing unit are mitigated, as discussed in ref. 42, with water content incorporated alongside temperature and the catalyst-to-oil ratio in the proposed conversion-activity correlation.

## 4. Conclusions

This study systematically examined the effects of cofeeding water and methanol on the catalytic cracking of Arabian light crude oil over a broad range of operating conditions using a micro-activity testing (MAT) unit, supported by kinetic modeling. This work provides detailed insights into how these cofeeds alter reaction selectivity, coke formation, and intrinsic kinetic parameters, with implications for industrial cracking optimization. The main conclusions are:

- Thermal reaction effects
  - Water and methanol cofeeding at 525 °C increased the propylene-to-ethylene ratio and strongly suppressed coke formation.
  - At 625 °C, both additives enhanced conversion, increased CO and CO<sub>2</sub> yields, and elevated the olefin-to-

paraffin ratio, although the latter decreased when methanol was cofed with water.

- Water and methanol promoted isomerization reactions in both gas and liquid phases, and increased the olefin-to-aromatic ratio in liquids under thermal conditions.
- Monomolecular cracking
  - Cofeeding water or water-methanol mixtures enhanced conversion and propylene-to-ethylene ratios at low catalyst-to-oil ratios, particularly at higher temperatures.
  - Kinetic modeling confirmed that water cofeeding increased the rate constant for the monomolecular cracking pathway to propylene across the entire temperature range.
- Bimolecular reactions and coke suppression
  - Water and methanol cofeeding significantly reduced coke formation at high catalyst-to-oil ratios, improving catalyst activity.
  - Water addition suppressed condensation reactions responsible for coke precursor formation while promoting hydrogen transfer in heavy fractions and isomerization in light fractions.
- Methanol-specific effects
  - Methanol cofeeding enhanced isomerization more than water alone under both thermal and most catalytic cracking conditions, with a stronger effect at high severity and temperature.
  - Methanol favored alkylation of benzene to toluene and xylenes at low temperatures and catalyst-to-oil ratios, attributed to methyl radical formation.
  - Increasing methanol content beyond ~30 vol% led to higher coke and HC-lump yields with relatively small gains in light olefins, due to increased methane production.
  - Within the studied high-temperature range, methanol cofeeding did not improve olefin selectivity relative to paraffins and, in some cases, shifted selectivity toward paraffins.

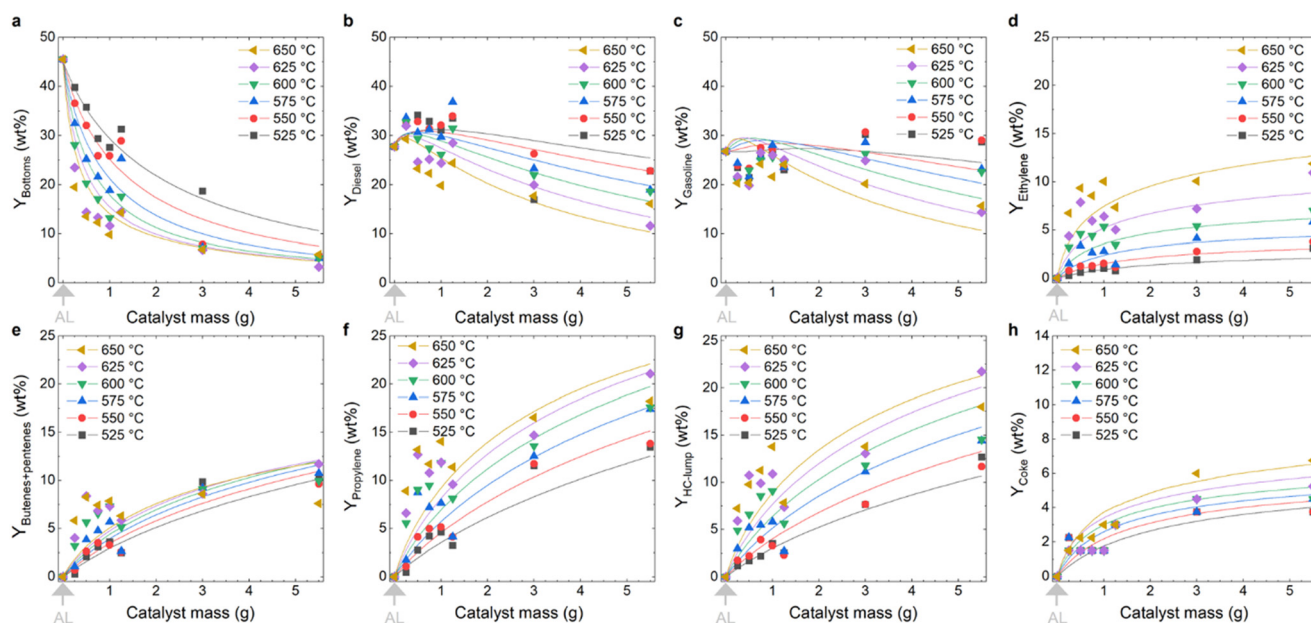


Fig. 7 AL + W(0.2) data points (scattered) and the predicted yields (solid curves).



- Kinetic model implications

- Reparameterization with water cofeeding data showed correlated changes in kinetic parameters for most reactions, except diesel → bottoms, bottoms → coke, and bottoms → ethylene.

- The model achieved good agreement with experimental data ( $R^2 = 0.92$ ) and is suitable for integration into multiphase simulations when including a water-content term in the conversion–activity correlation.

Overall, the combined experimental–modeling approach confirms that water cofeeding can beneficially influence FCC operation by enhancing monomolecular cracking, mitigating coke formation, and shifting selectivity, while methanol cofeeding offers selective benefits in isomerization and aromatic alkylation but does not improve light olefin selectivity at high temperatures.

## Conflicts of interest

There are no conflicts to declare.

## Data availability

The datasets generated and analyzed during this study—including raw MAT reactor outputs, gas chromatography data, coke quantification measurements, and kinetic model input–output files—are available from the corresponding authors upon reasonable request. Due to institutional data management policies and ongoing related research activities, the full experimental dataset cannot be made publicly available at this time. All data necessary to reproduce the figures, kinetic parameter fitting, and conclusions of this work are provided within the article and its supplementary information (SI).

Supplementary information is available. See DOI: <https://doi.org/10.1039/d5re00525f>.

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