Supplementary Information: Quantitative Carbon Detector (QCD) for Calibration-Free, High-Resolution Characterization of Complex Mixtures

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Summary. This supplementary material section supports the data and conclusions presented in the main body of the paper. It contains calibration curves used to calculate the response factor of compounds analyzed using QCD and conventional FID. A description of the experiments used to confirm the absence of coking and to ensure complete combustion and methanation within the catalyst reaction chambers is also included. As is a description of the catalyst loading methods and the PID settings used to operate the QCD.

Response Factors. Compound response factors were calculated for both the QCD and FID by plotting peak area (scaled by a methane internal standard) versus moles of carbon injected. A total of fifteen compounds were analyzed by the QCD to produce response factors (Fig. S1) while fourteen compounds were analyzed by the conventional FID (Fig. S2). The plotted data was linear with an $R^2 \geq 0.900$, with two exceptions: 2-methylfuran (QCD) and levoglucosan (FID). The QCD response factors are all similar, while the FID response factors vary over an order of magnitude.

Additional Experimental Details. Experiments were conducted to ensure complete oxidation/methanization and the absence of coking in the combustion and methanization reaction chambers. A range of oxygenated, aromatic, and alkyl compounds were used to simulate likely compounds present in unresolved complex mixtures (UCMs), including: n-heptane, methane, 2,6-dimethoxyphenol (DMP), and 3,4-dimethoxyacetophenone (DMAP). Coking in the combustion reaction chamber was tested by replacing the oxygen flow with an equivalent helium flow and injecting a sample of methane. After the methane peak eluted, the oxygen flow was turned back on. If any coking had occurred, the coke would have been combusted and an additional peak would have been observed. This was not the case, therefore coke was not forming in the combustion reaction chamber. To guarantee that combustion was reaching completion in the first reaction chamber, the flow of hydrogen to the second reaction chamber was replaced with helium and several different samples were injected. If combustion

was complete, the injected sample would be converted to CO_2 and no peak would be observed. During tests, no peak was observed, confirming that combustion was indeed complete. The same reaction conditions as those used to test for complete combustion (i.e. replacing hydrogen flow with helium) were used to test for coking in the methanization reaction chamber. CO_2 was injected and enough time to allow CO_2 to exit the QCD had passed, the hydrogen flow was turned back on. No peak was observed, indicating there was no coking in the reactor. Similarly, to test for complete methanization, separate samples of methane and CO_2 were injected. The two samples produced the same response, which confirmed that methanization was indeed complete.

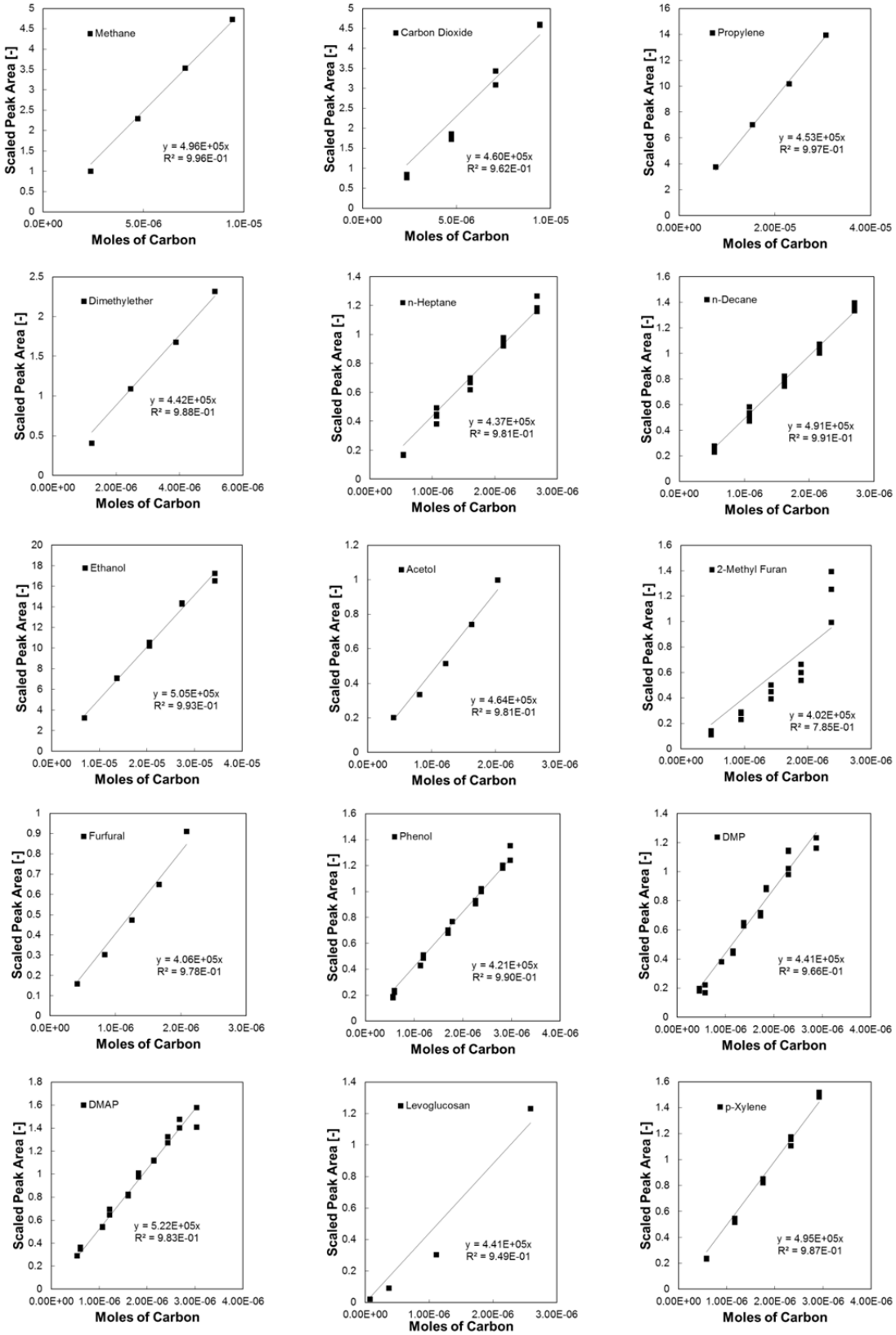

Figure S1. QCD response factor plots for fifteen compounds.

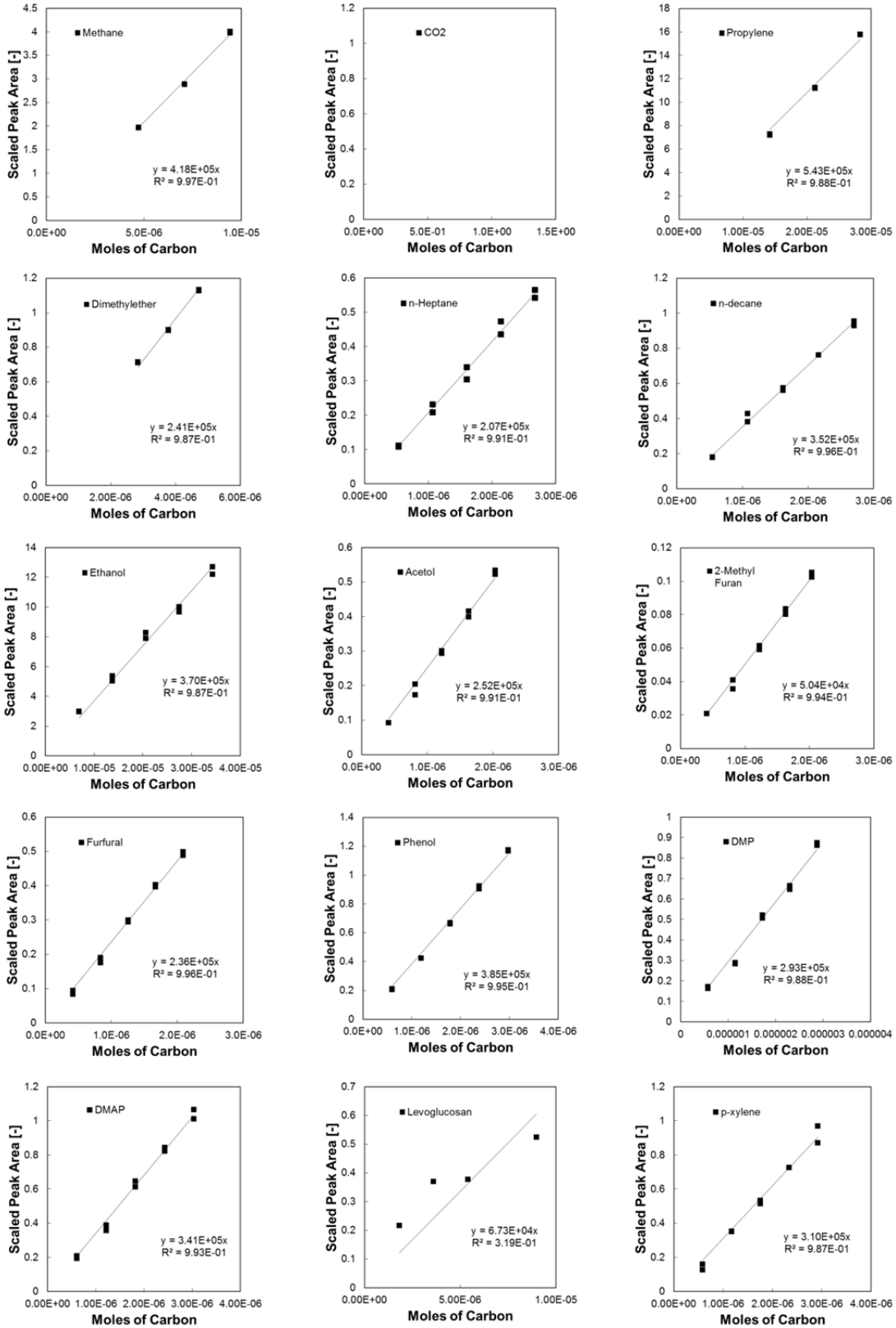

Figure S2. FID response factor plots for fourteen compounds.