

Supporting Information:

Catalytic naphtha reforming – a novel control system for the bench-scale evaluation of commercial continuous catalytic regeneration catalysts.

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Section 1 Gas and liquid sampling systems

On-line gas analysis description: A schematic representation of the product sampling system is given in Figure S1. The back pressure regulator is set at 2-3 bar to enable flow through the refinery gas analyzer (RGA) which can handle an inlet pressure of up to 17 bar. A T-piece is installed to take a part of the gas to the RGA. The line (L3) goes vertically up before it goes to the RGA to prevent liquid from entering the gas sampling system.

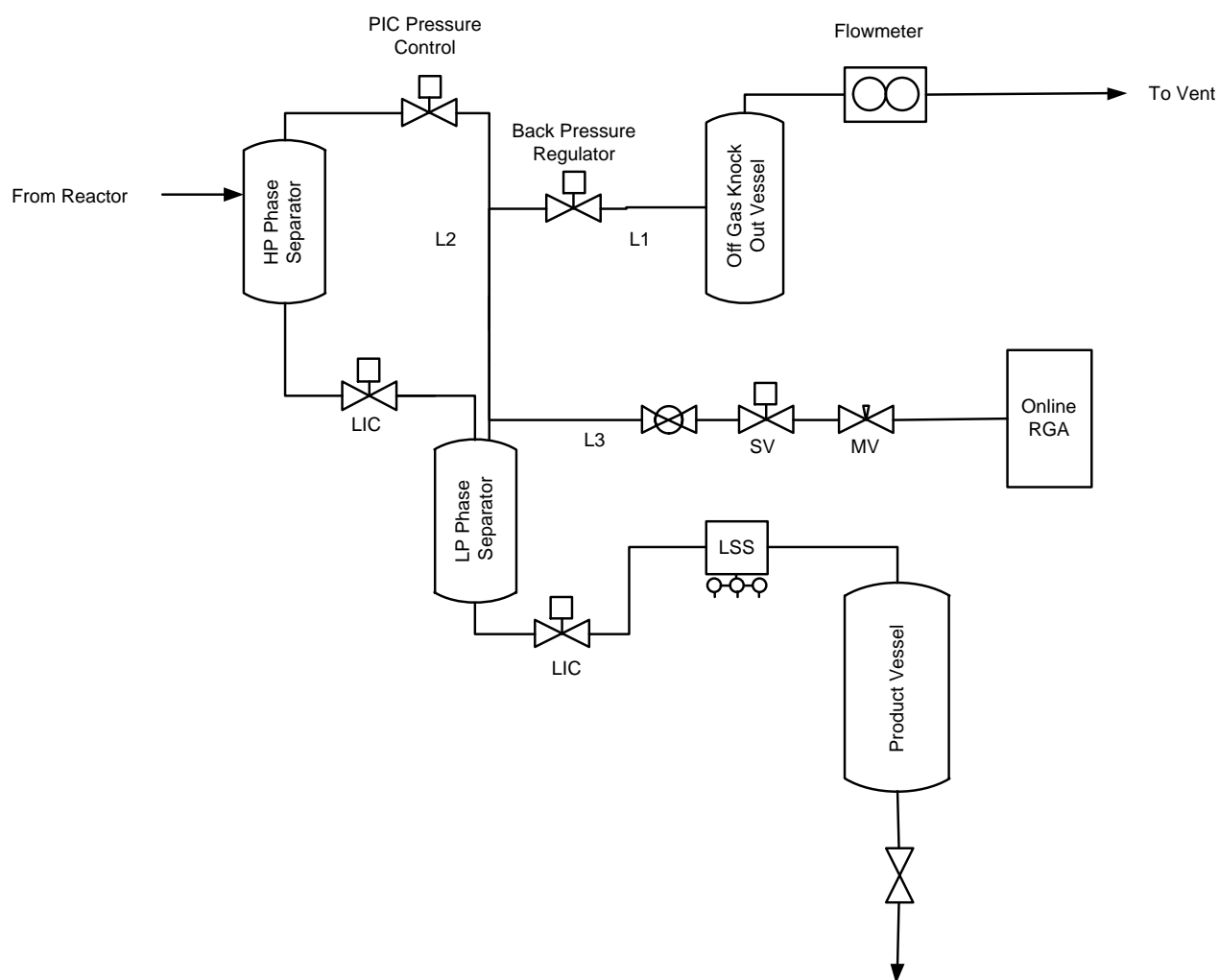


Figure S1. Simplified process flow diagram of the off-gas & liquid analysis systems

The ball valve on the line isolates the RGA as well as a selector valve (SV) used as a solenoid followed by a metering valve (MV) to control the flow to the RGA. The metering valve is set at a flow that does not affect the pressure or mass balance of the system while being sufficient to ensure the lines are purged and free of contamination. The system is programmed with the Agilent scheduler program to open the selector valve at the chosen frequency (typically hourly). The scheduler then automatically purges the line for a minute and then takes the sample. It then initiates the RGA analysis after the sample has been taken, while it closes the selector valve at the same time as to prevent the loss of any unnecessary gas.

Semi-automated liquid analysis description: A 12-port selector valve (LSS in Figure S1) is installed before the product pot. The liquid product enters the valve system and flows continuously through the valve. The dotted lines indicate the path taken by liquid when port 1 is opened. The selector valve is then programmed to change between ports 1-12 at selected times using the Agilent scheduler system, which allows for a small amount of product to be left in the sample loop. Each sample loop consists of 1/8" lines, ball valve and a 1/4" T-piece to increase the volume of the sample and ensure a sufficient volume for GC analysis is collected. It should be noted that the small liquid hold-up in the lines does not affect the mass balance as it has already been measured through the Coriflow meter. A 1/8" 3-way valve is found before the selector valve to select between in-line process product and nitrogen. The nitrogen flow is controlled by a 1/8" metering valve. When the sample from any loop needs to be transferred to a GC vial, it is possible to switch to nitrogen and manually select the valve position of the loop to be drained. Opening the ball valve on the selected loop then forces out the sample into the GC vial.

When the sample loop has been purged for approximately 30 seconds the next loop is selected. The filled GC vials are then loaded and queued on the GC-FID auto sampler system. A detailed schematic representation of the valve system is shown in Figure S2.

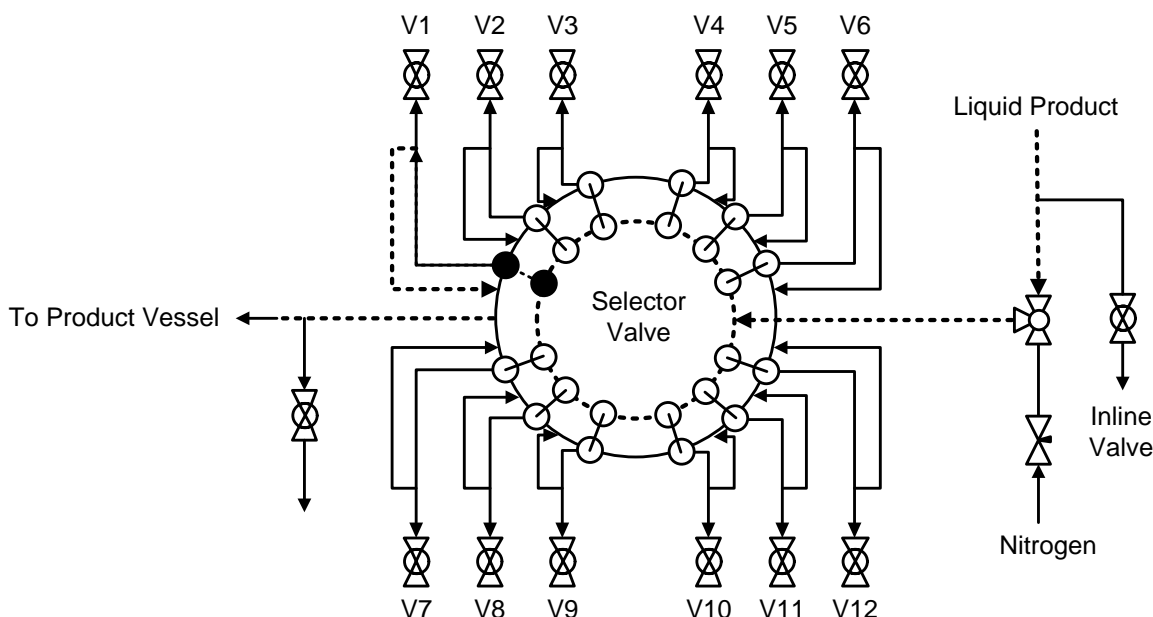


Figure S2 Schematic representation of the liquid sampling valve system.

Section 2 Algorithm for controlling of catalyst bed temperature profiles

The algorithm consists of three basic steps i.e. 1) identifying the model, 2) inverting the model mathematically and 3) solving the inverted model for the desired reactor bed temperature profile.

Identifying the model Firstly the relation between the wall temperatures and internal bed temperatures is estimated. Since there are exothermic and endothermic reactions occurring simultaneously in a reactor bed, this relation is not expected to be linear, but it is found that it can be sufficiently modeled by a linear difference equation. A k^{th} order model is therefore generated to approximate this wall-bed relationship at a fixed bed temperature state.

The relationship between the manipulated and controlled variables needs to be found. Let the bed temperatures be the controlled variables and the wall temperatures be the manipulated variables. It is assumed that there are no deviation variables.

Let $Y(k)$ be defined as a vector of the m reactor bed temperatures, and $U(k)$ the vector of the n reactor wall temperatures at some discrete sampling time k :

$$Y(k) = \begin{bmatrix} y_1(k) \\ y_2(k) \\ \vdots \\ y_m(k) \end{bmatrix}, U(k) = \begin{bmatrix} u_1(k) \\ u_2(k) \\ \vdots \\ u_n(k) \end{bmatrix} \quad (1)$$

Let the reactor model be a linear difference equation of order L given by

$$Y(k+1) = \sum_{i=0}^{L-1} (A_i Y(k-i) + B_i U(k-i)) + C \quad (2)$$

Where:

i, k are integers,

$A_i \in R^{m \times m}, B_i \in R^{m \times n}, C \in R^{m \times 1}$ are the coefficient real matrices.

L is an integer and also the estimated order of the difference equation.

A least squares approximation is then used to fit the model (Eq.2) to the data, for the estimation of the coefficient matrices.

Deriving the model inverse The linear dynamic model is simplified and converted to a steady-state model, to predict how the reactor will behave from a steady-state to another. If $U(k) = U_\infty$ is kept constant in Eq.2, assuming that the model is stable, then $Y(k) \rightarrow Y_\infty$ as $k \rightarrow \infty$. We can now simplify Eq.2 as follows in order to derive the steady-state model of the reactor:

$$Y_\infty = \sum_{i=0}^{k-1} A_i Y_\infty + \sum_{i=0}^{k-1} B_i U_\infty + C \quad (3)$$

Let $A = \sum_{i=0}^{k-1} A_i$ and $B = \sum_{i=0}^{k-1} B_i$, and if the inverse of $I - A$ exists, I being the identity matrix, then

$$Y_{\infty} = AY_{\infty} + BU_{\infty} + C$$

$$Y_{\infty} = (I - A)^{-1}BU_{\infty} + (I - A)^{-1}C$$

If we let $K_p = (I - A)^{-1}B$ and $K = (I - A)^{-1}C$, then

$$Y_{\infty} = K_p U_{\infty} + K \quad (4)$$

Lastly the model is inverted, so that for a given bed temperature profile, a wall temperature profile can be estimated, and thereby solving the control problem.

If Eq.4 is rearranged, solving for U_{∞} , using the Moore-Penrose pseudo-inverse¹, it follows that:

$$U_{\infty} = K_p^{-1}(Y_{\infty} - K) \quad (5)$$

Implementation of the algorithm To implement this algorithm Eq.5 is used, where the user will select some desired reactor bed-profile $Y_{setpoint}$ substitute this in Y_{∞} to calculate U_{∞} . The values of U_{∞} are then used as the set-points of the reactor bed heaters. This system was extended to an automated system that updates the model; write the result to the distributed control system (DCS), and thereby controlling the system continuously. In this application, the model was constructed (all coefficients computed) during a “modeling run” using a standard catalyst, loading diagram and process conditions. The modeling run’s temperature data was only collected after feed was introduced to the reactor system as to incorporate the flow dynamics of the feed. The average bed temperature was also varied over the expected temperature range (480-520 °C) to ensure that coefficients are representative. The desired reactor temperature profile was then inserted for subsequent runs and the DCS allowed to automatically control the heater set-points. Setting the desired bed temperatures to all be equal, resulted in near iso-thermal operation.

Section 3 Further examples with data from iso-thermal and iso-RON studies

Figure S3 shows two non-consecutive iso-thermal runs using the same catalyst and feed combination repeated within 30 days. Table S1 gives data from three three Iso-RON studies

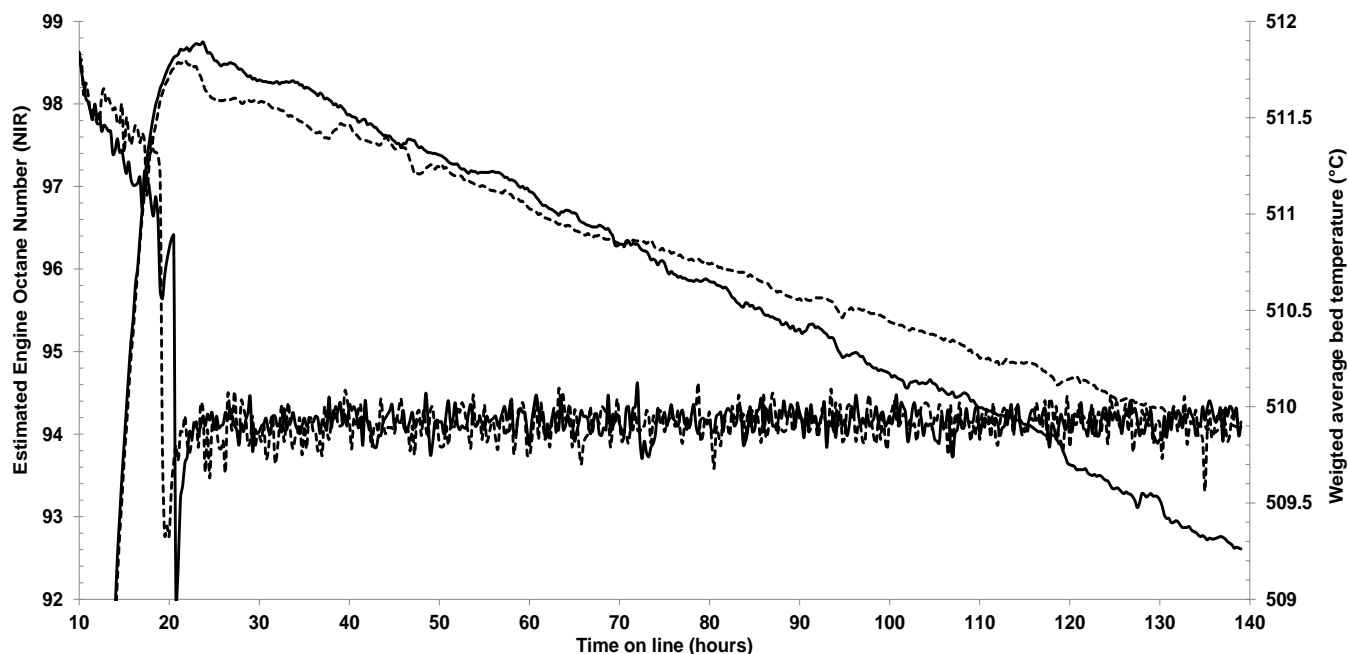


Figure S3. Iso-thermal study at 510 °C repeated within 30 days. LHSV = 2.5 h⁻¹, H₂/oil molar ratio = 3, pressure = 9 barg. Legend: (—) Run1; (----) Run 2

Section S4 Details of chromatographic methods

RGA method The GC data was collected using an Agilent Technologies 7890A RGA gas chromatograph using the following method:

GC injector: (GC valve)

Gas Sampling Valve; GSV Loop volume: 1mL; Load time: 0.1 min; Inject time: 0.2 min

Inlet:

Mode: split; Initial temperature: 200°C; Pressure: 205 kPa; Split ratio: 150:1; Total flow: 867.9 ml/min; Gas Type: Helium

Column:

HP-Pona Methyl Siloxane 35 m x 320 μm x 8 μm Agilent; ; Mode: constant flow; Flow: 5.7 ml/min; Nominal initial pressure: 205 kPa; Average velocity: 71.4 cm/sec

Oven:

80 °C initial temperature; 3.0 minute hold; 35 °C/min ramp to 185 °C; 2.2 minute hold time

Front Detector:

FID; Temperature: 220 °C; Hydrogen flow: 35.0 ml/min; Air flow: 350.0 ml/min

Back Detector:

TCD; Temperature: 155 °C; Reference flow: 18.0 ml/min

Integration events:

Slope selectivity: 10.000; Peak width: 0.013; Area reject: 0.010; Height reject: 0.010; Shoulders: off

GC-FID method The GC data was collected using an Agilent Technologies 6850 GC-FID gas chromatograph using the following method:

GC injector: (autosampler)

Injection volume: 0.2 µl

Inlet:

Mode: split; Initial temperature: 250°C; Pressure: 34.1 kPa; Split ratio: 140:1; Total flow: 143.3 ml/min; Gas Type: Nitrogen

Column:

HP-1 Methyl Siloxane 30 m x 320 µm x 0.25 µm Agilent 19091Z-413E; Mode: constant flow; Flow: 1.0 ml/min; Nominal initial pressure: 34.1 kPa; Average velocity: 19 cm/sec

Oven:

50°C initial temperature; 2 minute hold; 2°C/min ramp to 100 °C; 2-minute hold time; 4°C/min ramp to 170 °C; 2-minute hold time; Run time: 48.5 min

Detector: FID

Temperature: 250°C; Hydrogen flow: 40.0 ml/min; Air flow: 450.0 ml/min; Mode: constant column+ makeup flow; combined flow: 50.0 ml/min; Makeup gas: nitrogen

Integration events:

Slope selectivity: 50.000; Peak width: 0.040; Area reject: 1.000; Height reject: 1.000; Shoulders: off

Table S1 Three Iso-RON studies with yield and reformat composition/property data collected for three commercial CCR type catalysts (LHSV = 3.00 hr⁻¹, H₂/oil = 3 mol/mol, P = 9 bar).

| Property Measured | Catalyst A | | Catalyst B | | Catalyst C | |
|--|------------|----------|------------|----------|------------|----------|
| | Average | δ | Average | δ | Average | δ |
| Adjusted GC RON | 95.6 | 0.2 | 95.5 | 0.2 | 95.6 | 0.1 |
| Adjusted GC MON | 85.2 | 0.1 | 85.2 | 0.1 | 85.3 | 0.1 |
| GC estimated RON | 97.6 | 0.1 | 97.5 | 0.1 | 97.6 | 0.1 |
| GC estimated MON | 85.7 | 0.1 | 85.7 | 0.1 | 85.8 | 0.1 |
| CFR Engine RON | 95.8 | 0.3 | 95.6 | 0.3 | 95.6 | 0.3 |
| WABT @ RON95 (°C) | 507.0 | 0.1 | 499.5 | 0.1 | 499.6 | 0.1 |
| Mass balance | 99.9 | 0.5 | 99.9 | 0.7 | 99.8 | 0.4 |
| Total aromatics | 66.2 | 0.3 | 65.8 | 0.3 | 65.9 | 0.2 |
| Benzene | 2.0 | 0.0 | 1.9 | 0.0 | 2.0 | 0.0 |
| Toluene | 12.6 | 0.1 | 12.9 | 0.1 | 12.8 | 0.1 |
| Ethyl benzene | 4.4 | 0.0 | 4.3 | 0.0 | 4.4 | 0.0 |
| Total xylenes | 18.3 | 0.1 | 18.2 | 0.1 | 18.2 | 0.1 |
| Total C ₉ aromatics | 21.3 | 0.1 | 21.0 | 0.1 | 21.0 | 0.1 |
| Total C ₁₀ ⁺ aromatics | 7.7 | 0.1 | 7.6 | 0.0 | 7.5 | 0.0 |
| Measured density (20 °C) | 0.788 | - | 0.787 | - | 0.787 | - |
| Normalised H ₂ yield | 3.0 | 0.1 | 3.0 | 0.1 | 2.8 | 0.1 |
| Normalised LPG yield | 11.9 | 0.1 | 12.6 | 0.1 | 12.4 | 0.1 |
| Normalised C ₁ yield | 1.0 | 0.0 | 1.0 | 0.0 | 1.1 | 0.0 |
| Normalised C ₂ yield | 2.6 | 0.0 | 2.8 | 0.0 | 2.8 | 0.0 |
| Normalised C ₃ yield | 3.4 | 0.1 | 3.7 | 0.1 | 3.5 | 0.0 |
| Normalised C ₄ yield | 4.8 | 0.1 | 5.1 | 0.1 | 5.0 | 0.1 |
| Normalised C ₅ ⁺ yield | 85.2 | 0.2 | 84.4 | 0.2 | 84.8 | 0.1 |

REFERENCE

(1) MATLAB, version 7.10.0 (R2010a), The MathWorks Inc. Natick, Massachusetts 2010.